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## **Removal of Contaminants from Fine Grained Soils Using Electrokinetic (EK) Flushing**

**Final Report  
September 30, 1987 - June 30, 1993**

**B. E. Reed  
M. T. Berg**

October 1993

Work Performed Under Contract No.: DE-FC21-87MC24207

For  
U.S. Department of Energy  
Office of Fossil Energy  
Morgantown Energy Technology Center  
Morgantown, West Virginia

By  
West Virginia University  
National Research Center for Coal and Energy  
Morgantown, West Virginia

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## EXECUTIVE SUMMARY

Recently, attention has focused on developing cost effective techniques to remove inorganic contaminants from soils *in-situ*. For most *in-situ* techniques hydraulic pressure (*i.e.*, pumping) is used to disperse the chemical additives and collect the contaminated groundwater. *In-situ* treatment technologies have had success at sites containing sandy soils but have not shown much promise for soils with large amounts of clay and silt (*i.e.* fine grained, low hydraulic conductivity soils). This is due primarily to difficulty in transporting groundwater, contaminants, and chemical additives through the subsurface. Unfortunately, soils high in clay and silt are known to sequester large quantities of inorganic and organic contaminants. Thus, soils having low hydraulic conductivity's are generally efficient in sequestering pollutants but are resistant to standard *in-situ* remediation techniques because of the difficulty in transporting groundwater and contaminants. A candidate technology for the *in-situ* remediation of low permeability soils is electrokinetic (EK) soil flushing. In EK soil flushing, groundwater and contaminants are transported under an applied voltage. The transport of groundwater electroosmotically (*i.e.*, under an applied voltage) does not depend directly on the soil's hydraulic conductivity. Thus, soils that would otherwise require excavation and treatment can be remediated *in-situ* if electrokinetics is used as the driving force for liquid and contaminant transport.

This report details the results from work conducted on the use of EK soil flushing to remediate a fine grained (low permeability) soil contaminated with lead. The first portion of the experimental work entailed soil collection and characterization, soil adsorption and desorption of lead, and EK reactor construction and testing. The second phase of the research consisted of investigating the efficacy of using EK soil flushing on an actual soil using bench-scale EK reactors. For the second phase of the research the affect of initial conditions (lead contamination levels, reservoir conditioning, and applied voltage) on the efficiency of EK soil flushing was studied.

Test soil was collected from a site in Northern Erie County, New York and underwent standard preparation and physical/chemical characterization. Based on the Soil Conservation Service classification, the soil is a silt loam. The soil has a low hydraulic permeability ( $<10^{-7}$  cm/s), has a large amount of fine materials, moderate organic carbon content, and a moderately high cation exchange capacity (CEC). The soil has a low indigenous lead content and is slightly acidic.

The study soil was artificially contaminated, in the batch mode, with lead to concentrations of 95, 800, and 7600 mg Pb/kg soil. Laboratory determined soil lead concentrations agreed well (within 10 percent) with those calculated from mass balance calculations. Lead batch desorption experiments were conducted using several concentrations of HCl, HNO<sub>3</sub>, EDTA, CaCl<sub>2</sub>, acetic acid, and tap water. HCl, HNO<sub>3</sub>, and EDTA desorbed the majority of the soil-bound lead. Acetic acid and CaCl<sub>2</sub> were less effective while, tap water was ineffective. Based on these results, several of these reagents (HCl, EDTA, acetic acid, NaNO<sub>3</sub> in place of CaCl<sub>2</sub>) were added to the reservoir waters of the EK reactor to attempt to improve remediation efficiency. The remainder of the experimental work had as its focus this goal.

Water movement during EK soil flushing of a lead contaminated soil was evaluated as a function of EK operating conditions (initial lead concentration (related to initial soil water conductivity), reservoir conditioning (NaNO<sub>3</sub>, acetic acid, HCl), and applied voltage (30 or 60 V)) using the following parameters: Volume of water transported per day, the average current for the duration of the experiment, the volume of soil water transported per amp-hour ( $K_j$ ), and the number of kW-hr required to pump one gallon. In all cases, both the flow rate and current increased when the initial lead concentration (and thus soil water conductivity) was increased. An increase in the reservoir waters' conductivity increased both flow and current. Buffering the cathode reservoirs with either NaNO<sub>3</sub> or acetic acid (HAc) while conditioning the anode reservoir with NaNO<sub>3</sub> produced the highest flow rates. Voltage had the largest influence on both the flow rate and current. Increasing the voltage from 30 to 60 V produced a 230 to 330 percent increase in flow and between a 90 and 230 percent increase in current. Increasing the voltage did not cause a noticeable increase in soil temperature or further soil consolidation. In future work, larger voltages should be investigated to determine if an optimum voltage exists.

$K_j$  and  $E_T$  are measures of how efficient water is transported under an applied voltage.  $E_T$  can be used to compare power costs required for pumping between different operating conditions. A larger  $K_j$  and a smaller  $E_T$  correspond to more efficient water movement. For all cases, the standard deviation from the mean and the coefficients of variation for  $K_j$  and  $E_T$  were smaller than those observed for the flow rate and current because the dependence of flow on current is taken into account when calculating  $K_j$  and  $E_T$ . Thus, determining the effect of initial conditions on electroosmotic (EO) flow may be more reliable if  $K_j$  and  $E_T$  are used. At higher soil Pb concentrations (soil water conductivity), EO flow was more efficient (larger  $K_j$  and smaller  $E_T$ ) for 1000 mg/kg Pb (1400-2000  $\mu\text{mho}$ ) compared with 150 mg/kg Pb (650-850  $\mu\text{mho}$ ). Reservoir conditioning had a less noticeable effect on  $K_j$  and  $E_T$ . An exception was the test where 0.1 N HCl was used to condition the anode. This test had a much lower  $K_j$  and much higher  $E_T$ . During the HCl test, Cl<sub>2</sub> (g) was detected olfactory sense. The production of Cl<sub>2</sub> (g) from Cl<sup>-</sup> requires energy thus, Cl<sub>2</sub> (g) formation could significantly affect  $K_j$  and  $E_T$ . The production of Cl<sub>2</sub> (g) could also present a health and safety problem.

Increasing the voltage increased the volume of water transported per amp-hr ( $K_j$ ) but increased the power required per gallon ( $E_T$ ). The increase in power costs may be offset by a decrease in other costs (personnel, monitoring, *etc.*) resulting from a decrease in time required to remediate the site.

Lead removal and soil pH from the soil during EK soil flushing were also evaluated as a function of initial operating conditions. For tests that did not have cathode reservoir pH control, the pH of the soil segment next to the cathode was higher than the initial pH (pH  $\approx$  8.5 to 9 compared with pH<sub>initial</sub>  $\approx$  6.5). The OH<sup>-</sup> produced from electrolysis of water in the cathode was transported in the direction opposite of advection by diffusion and ion migration. The OH<sup>-</sup> that is transported into the soil precipitated with the desorbed lead and increased the likelihood of adsorption. Thus, the overall remediation efficiency was decreased. If long EK flushing durations are used, there will be sufficient transport of H<sup>+</sup> to lower the soil pH at the cathode.

There appeared to be a correlation between the soil pH and the onset of lead removal. When the pH was reduced to below 4, lead was desorbed from the soil. When the pH was above this critical pH, the soil lead concentration was equal or greater than the initial Pb concentration. While the basis for EK flushing termination in the field will be the contaminant soil concentration, these results indicate that the extent of contaminant movement in the field can be assessed day-to-day by monitoring the soil pH. This would result in significant cost savings from the reduction in sampling and analytical services. The  $pH_{critical}$  is most likely a function of soil and contaminant type thus, it would require determination of site specific parameters. In the future, with additional research and model development, the  $pH_{critical}$  may be calculated by examining the soil and contaminant characteristics.

For the majority of the tests that had 1 M acetic acid (HAc) conditioning of the cathode reservoir, the pH of the last soil section was less than 4. The pHs of the cathode reservoir liquid for these tests were between 2.3 and 4.6 for the duration of the experiments. However, the pH of the cathode soil was not significantly lower than the initial soil pH (6.5 - 7) unless there was substantial water movement. This indicates that for acetic acid conditioning, significant decreases in soil pH results from the movement of  $H^+$  from the anode, not from the cathode. Thus, buffering of the cathode reservoir was most effective if sufficient water movement occurs. Buffering the cathode with 1 M HAc also allowed the desorbed lead to be transported into the cathode reservoir (thus, the soil is truly remediated). For tests that did not have HAc conditioning of the cathode, the desorbed lead resided in the soil near the cathode. Eventually, the  $H^+$  front would have swept across the entire soil sample, lowering the soil pH at the cathode so that the precipitated/sorbed lead could move into the reservoir. However, this would require a long period of time to occur.

The best removal of lead occurred when HCl was added to the anode reservoir. In one case, 80 percent of the soil-bound lead was removed from 100 percent of the soil (by weight) while 45 percent of the soil (by weight) had more than 95 percent of the lead removed. The HCl tests also had the largest  $E_T$  (power costs). However, the increase in power costs could be off-set by the decrease time required for remediation. Additional research is required before an optimum EK soil flushing design can be determined.

In summary, EK soil flushing appears to be a promising *in-situ* remediation technique. Significant quantities of lead were removed from the soil in a relatively short period of time when the cathode reservoir was pH controlled. For the tests where there was no pH control, much longer durations were required to move similar amounts of lead. Voltage also strongly affects remediation efficiency. Increasing the voltage from 30 to 60 dramatically increased the efficiency of the EK soil flushing process.

## 1. INTRODUCTION

Recently, attention has focused on developing cost effective techniques to remove inorganic contaminants from soils *in-situ*. An example of this technology is *in-situ* soil washing. *In-situ* soil washing promotes contaminant solubilization and migration in the liquid phase so that the contaminants can be flushed from the subsurface. Chemicals, such as acids or chelating agents, may be added to the soil system to increase the efficiency of the solubilization step. Hydraulic pressure (*i.e.*, pumping) is used to disperse the chemical additives and collect the contaminated groundwater. *In-situ* treatment technologies, such as *in-situ* soil washing, have had success at sites containing sandy soils but have not shown much promise for soils with large amounts of clay and silt (*i.e.* fine grained, low hydraulic conductivity soils). This is due primarily to difficulty in transporting groundwater, contaminants, and chemical additives through the subsurface. Unfortunately, soils high in clay and silt are known to sequester large quantities of inorganic and organic contaminants. Thus, soils having low hydraulic conductivity's are generally efficient in sequestering pollutants but are resistant to standard *in-situ* remediation techniques. **What is needed are cost effective and efficient technologies that can be used to remediate low permeability soils *in-situ*. A candidate technology for the *in-situ* remediation of low permeability soils is electrokinetic (EK) soil flushing.** In September of 1992, the Morgantown Energy and Technology Center (METC) provided funding to investigate the use of EK soil flushing in the remediation of a lead contaminated soil. The research was conducted using bench-scale EK reactors. Results from this preliminary study are encouraging and are the focus of this research report.

## 2. PURPOSE

The purpose of the proposed research was to study electrokinetics as a method of remediating contaminated soils *in-situ*. For this study, lead was chosen as the study contaminant because of its wide spread existence at hazardous waste sites. The research had as its objective the lab-scale testing of the electrokinetic process to determine the parameters that influence the transport of water and contaminants in a soil-groundwater system under an applied electric field. Specific tasks that were completed during the one year project are listed below.

**Task 1:** An extensive literature review on the electrokinetic phenomenon was conducted.

**Task 2:** Selection/characterization of soil, contamination of soil with lead, and soil washing tests.

**Task 3:** Electrokinetic (EK) reactor design, construction, and testing.

**Task 4:** Remediation of an actual soil (synthetically contaminated with lead), using electrokinetic soil flushing. Methods of electrode reservoir water conditioning that promote metal transport into the cathode reservoir were developed and compared.

**Task 5:** Initiated development of a theoretical model that will predict water and contaminant movement during EK soil flushing.

### 3. BACKGROUND

When an electric field is applied to a system having charged particles three mass transport phenomena can occur: electroosmosis, electrophoresis, and electrolytic migration. A schematic of the process for a soil system is presented in Figure 3.1. Electroosmosis (EO) is the movement of a liquid under an applied electric field, electrophoresis is the movement of a charged colloid under an applied electric field, and electrolytic migration is the movement of ions under an applied electric field. If the system is compacted (*e.g.*, soil system), electrophoresis is not usually a dominant phenomenon. Thus, for a contaminated site, electroosmosis and electrolytic migration are the principal transport phenomena. The term "electrokinetics" will be used in this report to mean the transport of contaminants via both electroosmosis and electrolytic migration. Contaminants are also subjected to diffusion driven transport. Diffusion of a chemical species occurs whenever a concentration gradient exists. In addition to these transport phenomenon, contaminants can undergo several types of reactions. These chemical reactions are divided into two classes; those that would occur in the absence of the applied electric field and those that occur because of the electric field.

In summary, the electrokinetic process is a complex set of physical, chemical, and electrical phenomena. While the electroosmosis process (*i.e.*, water movement) has been studied for decades, it is still not fully understood and a deterministic model to predict fluid and contaminant flow has not been developed and verified. The fate and transport of contaminants in a soil-groundwater system under an applied electric field is even less understood. However, based on a limited amount of research, using electrokinetics to remediate hazardous waste sites shows great promise. Thus, EK technology has the potential to be an integral part of the remediation of hazardous waste sites but additional research is required if the technology is to be applied in a rational way. Agencies having an interest in this type of research include the Departments of Energy and Defense, and the U.S. Environmental Protection Agency.

In the next sections, background information obtained during the completion of **Task 1** will be provided. The following topics are covered: electroosmotic movement of a liquid in a soil system, modeling the electrokinetic phenomenon (*i.e.*, **results from Task 5 of this research**), chemical reactions that occur during electrokinetics, and finally, a summary of the research conducted to date on the use of electrokinetics to remediate contaminated soils.

#### 3.1 ELECTROOSMOTIC WATER MOVEMENT

Electroosmotic technology has been used for decades for removing water from fine soils and sludges, stabilization of earthen embankments, and dewatering construction sites (Casagrande 1952, 1983). A primary driving force for developing electroosmotic technology was the inefficiency of using hydraulic pressure (*i.e.*, pumping) to induce fluid flow in low permeable soils.

As will be discussed in greater detail later, when an electric field is applied to a soil, a  $H^+$  front sweeps across the soil from the anode to the cathode. EO flow is dependent on soil surface electrochemistry (*i.e.*, pH, surface charge, *etc.*). Thus, a thorough understanding of surface

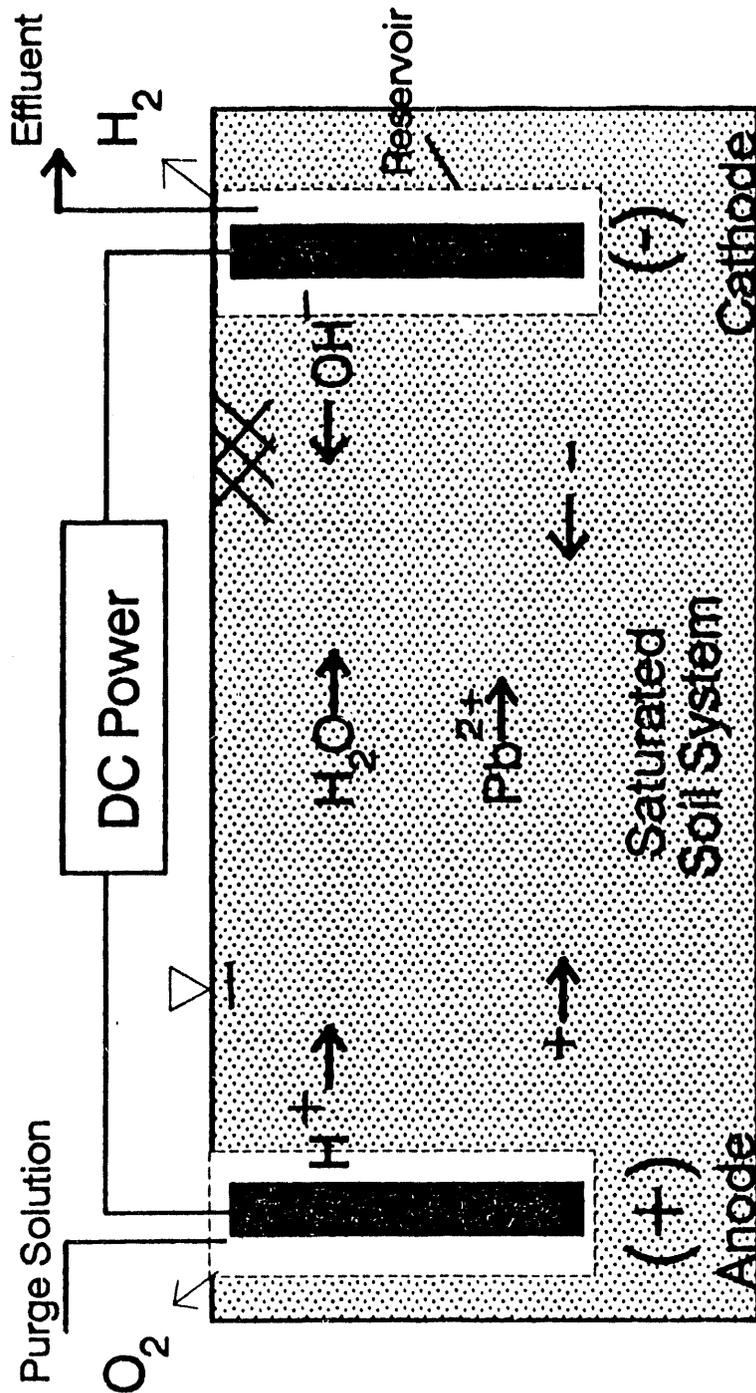


Figure 3.1. Schematic of the Electrokinetic Soil Flushing Process

behavior is important in understanding the electroosmotic/electrokinetic phenomenon. In this section, brief descriptions of the electrochemistry of charged surfaces and the various modeling approaches used to represent EO flow are presented.

### 3.1.1 Electrochemistry of Charged Surfaces

To understand EO water movement, one must first have an understanding of the electrochemistry of the soil surface and the soil pore water. Most soil surfaces are charged. In order to maintain electroneutrality, counterions will collect near the surface of the particle and extend in the solution forming an electric double layer (EDL). A schematic of a EDL for a negatively charged surface (*e.g.*, clays) is presented in Figure 3.2. The "ion cloud" is often divided into several sections based on the magnitude of the attraction between the surface and the ions. The counterions in the Stern Layer, are held more tightly than the ions in the diffuse layer. The potential at this plane (referred to as the "shear plane") is called the zeta potential. The zeta potential is used as a indirect measurement of the sign and magnitude of the surface charge and provides information on the EDL. The zeta potential is an important experimentally measured quantity. If the charge particle was placed in an electric field and was allowed to migrate (electrophoresis), a portion of the diffuse layer will be dragged along with the particle via frictional forces.

While surface chemists continue to debate on how the EDL should be divided, it is only important for this discussion to understand **that there exists a portion of the pore liquid that has an excess of counterions**. For a negatively charged soil surface, the counterions will be cations. Outside the ion cloud, the amount of charge associated with the cations must be equal to the amount of charge associated with the anions (*i.e.*, electroneutrality holds). When an electric field is applied to the soil system, anions will flow towards the positive electrode (anode) and cations will flow towards the negative electrode (cathode). As the ions move towards their respective electrodes, water is dragged along via momentum transfer (*i.e.*, frictional forces). Outside the EDL, the amount of water transferred towards the anode and cathode is equal (*i.e.*, net flow is zero). Inside the EDL, however, net flow is towards the cathode because there is an abundance of cations. Note, if the surface was positively charged, the reverse would occur (net flow towards the anode). It is apparent from this discussion that the magnitude and sign of the surface charge and the behavior of the EDL are of utmost importance in predicting the extent of EO flow. Parameters affecting surface charge include the type of soil components and the pH. Parameters affecting the EDL include the surface charge and conductivity. In the next several sections, surface charge development and the behavior of the EDL are discussed.

### 3.1.2 Surface Charge Development

As noted previously, most soil components possess a surface charge. Surface charges are classified as either permanent charges, which are typically negative, or as pH dependent charges, which can be positive or negative. A soil's net charge is the summation of both types of charges. Generally, clayey soils have a large abundance of negative charges, and soils with a high metal oxide content usually have an abundance of positive charges. Because EK flushing shows the most promise for clayey type soils, the discussion will focus on the formation of surface charge on

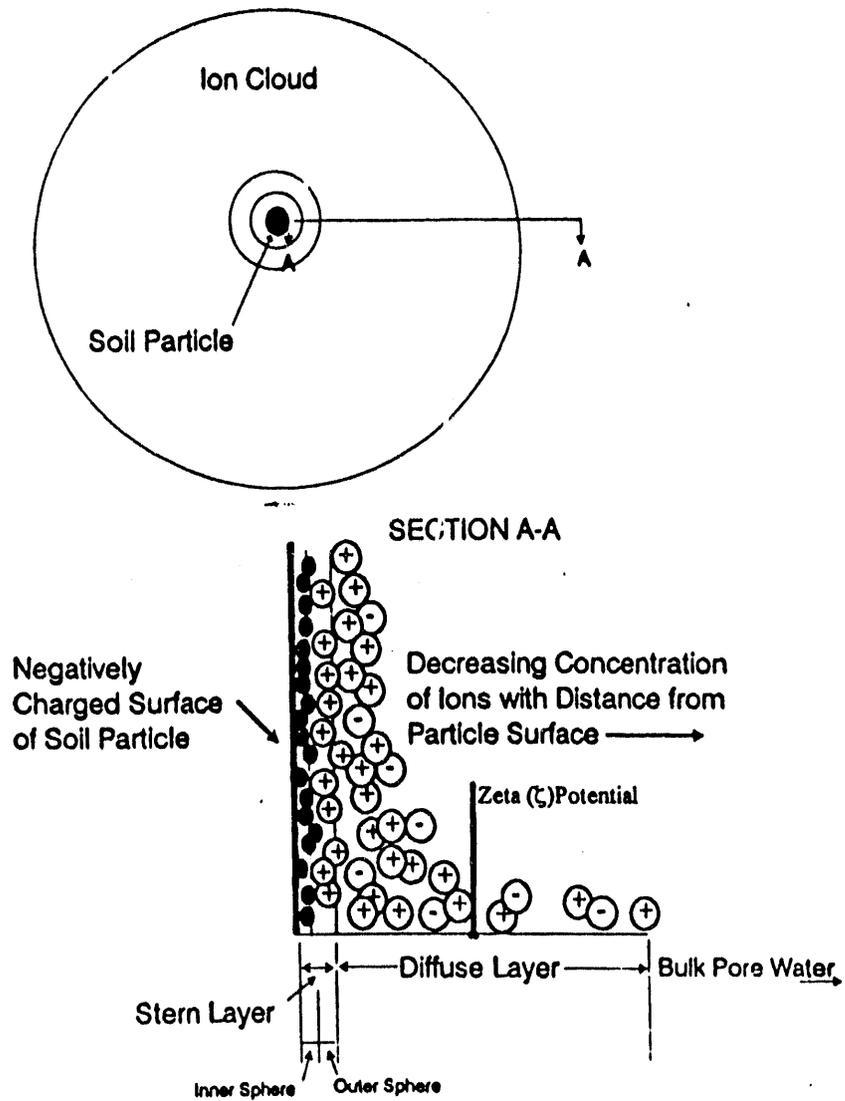


Figure 3.2. Schematic of the Electric Double Layer (EDL)

two general clay types: 2:1 and 1:1 clays. Schematic diagrams of these clays are presented in Figure 3.3. Because most actual soils are not pure clays, a description of other soil components that acquire a surface charge (metal oxides, organic matter) will be presented.

**2:1 Clays:** 2:1 clays, have two silica tetrahedral sheets sandwiching an aluminum octahedral sheet. This arrangement defines a unit layer for a 2:1 clay. Due to the crystal arrangement of 2:1 clays, the bonding between successive unit layers is relatively weak. Thus, the interlayer spacing can expand with the introduction of moisture (soil pore water), allowing ions in the soil pore water to replace other cations found in the unit layers of the mineral during the early stages of mineral formation. Such cation replacement is referred to as isomorphous substitution and only occurs with cations of comparable size and valence. Since the cation replacement occurs during formation, the resulting negative charge is considered to be permanent. The magnitude of the net permanent charge is related to the amount of substitution that took place. For example, a large portion of the negative charge found on montmorillonite is due to the substitution of  $Al^{3+}$  for  $Si^{4+}$  in the silica tetrahedral sheets or of  $Mg^{2+}$  for  $Al^{3+}$  in the octahedral sheet during mineral formation. The charge imbalance induced by these substitutions produces a net negative charge. Other 2:1 clays include vermiculite, illite, and mica. These clays are often referred to as "active clays" because of their shrink/swell behavior and their high cation exchange capacity (CEC, discussed in greater detail later).

**1:1 Clays:** A unit layer for a 1:1 clay consists of one silica tetrahedral sheet and one aluminum octahedral sheet. Successive unit layers are held together by O-OH bonds that produce relatively constant interparticle spacings that rarely expand. Due to the small spacing between layers, little isomorphous substitution can occur. Hence, the majority of the electrostatic charge that develops on 1:1 clays is caused by mechanisms other than isomorphous substitution and are pH dependent. pH-dependent charges generally develop on layer silicates when  $H^+$  ions dissociate from hydroxyl (OH) groups located on the mineral's edges or exposed planes. The dissociation of  $H^+$  from the OH groups of 1:1 clays, such as kaolinite, serves as the main source of negative charge on this group of layer silicates. pH dependent charges generally only comprise 5-10% of the total charge for 2:1 clays and 50% or more of the total charge for 1:1 clays (Bohn *et al.* 1979). Under acidic conditions, some hydroxyl groups of a 1:1 clay can adsorb protons ( $H^+$ ) to locally produce a positive charge, but all layer silicates possess a net negative charge (Evans 1989). However, if the clay particle is coated with a metal oxide (discussed in next section), a net positive surface charge can occur. 1:1 clays are referred to as "inactive clays" and generally have a much lower cation exchange capacity compared to active clays.

**Metal Oxides and Organic Matter:** Metal oxides, and organic matter have functional groups that can alter the charge of these particles by gaining or losing protons. Unlike permanent charges associated with isomorphous substitution, the surface charges developed by protonation or deprotonation are affected by soil pH and, hence, are referred to as pH dependent charges.

Most oxides, particularly those of iron, manganese, and aluminum behave amphotericly (positive charge at  $pH < pHzpc$ , negative charge at  $pH > pHzpc$ ). Surface hydroxyl groups act as a weak acid-base system. Surface reactions can be represented by (Evans 1989):

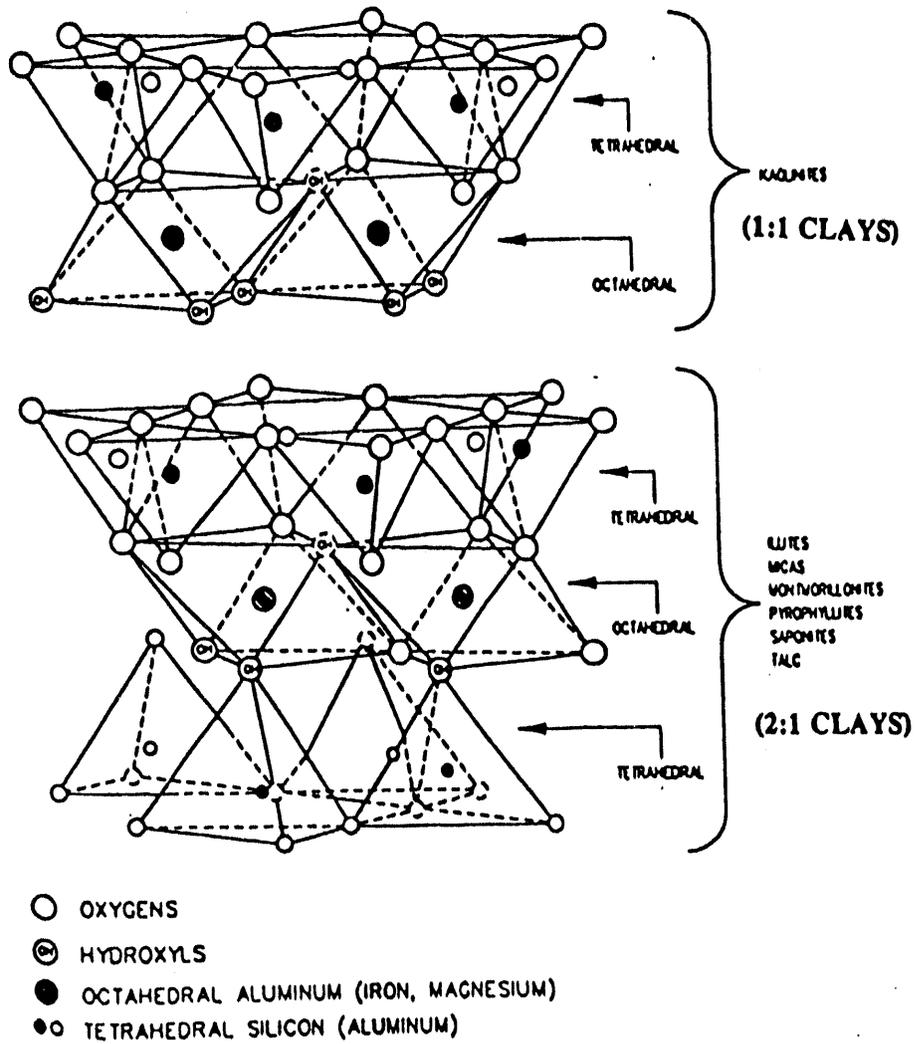
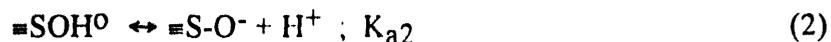
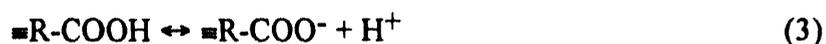


Figure 3.3. General Schematic Diagrams of 1:1 and 2:1 Layer Clays (Dragun 1988).



where [ $\equiv\text{S-}$ ] represents a metal oxide surface group. [ $\equiv\text{S-OH}_2^+$ ] and [ $\equiv\text{S-O}^-$ ] represent the protonated and deprotonated surfaces, respectively. The reactions in Equations 1 and 2 account for both the acid-base behavior and the surface charge of the soil. These reactions can be modeled using the Surface Complex Formation (SCF) model described by Reed and Matsumoto (1991). The  $\text{pH}_{\text{Zpc}}$  is the pH value at which the surface has a net zero charge. For  $\text{pH} < \text{pH}_{\text{Zpc}}$ , the soil surface has a net positive charge and for  $\text{pH} > \text{pH}_{\text{Zpc}}$  the surface has a net negative charge. In Equations 1 and 2, the  $\text{pH}_{\text{Zpc}}$  corresponds to the pH where the number of protonated and deprotonated surface sites are equivalent. Most Fe and Al oxides possess a  $\text{pH}_{\text{Zpc}}$  within the pH range of 6-9 while  $\text{MnO}_2$  typically has a  $\text{pH}_{\text{Zpc}}$  of 2-4.5 (Fergusson 1990). However, the actual  $\text{pH}_{\text{Zpc}}$  of naturally occurring compounds varies greatly. Amorphous allophanes have been found to have  $\text{pH}_{\text{Zpc}}$  values below pH 4 and as high as pH 6. Structural impurities and the aluminum: silica ratio of a soil are factors contributing to these variations (Greenland & Hayes 1978). As mentioned previously, metal oxides can coat the surface of soil particles, creating a second solid having characteristics quite different from the original particle.

The magnitude of the surface charge on organic matter is also pH dependent. Charge development on the organic fraction is mainly due to the ionization or dissociation of protons from carboxyl ( $\text{COOH}$ ), phenolic ( $\text{C}_6\text{H}_4\text{OH}$ ), and hydroxyl ( $\text{OH}$ ) surface groups (Alloway 1990). The following equation is used to represent the deprotonation of a carboxyl acid group that is a part of a humic or fulvic acid structure. The dissociation produces a negative charge on the organic surface group [ $\equiv\text{R-}$ ] (Evans 1989):



While positive charges can develop on the microscopic level, no soil organic fraction has ever been reported to have a *net* positive charge (Bohn *et al.* 1979)

**Determination of Surface Charge:** The surface charge of a hydrous solids can be estimated using a number of methods. The cation exchange capacity (CEC) is defined as the number of positive charges on the surface (measured in equivalents or milliequivalents) per mass of soil. In the same way, the anion exchange capacity measures number of negative charges on the surface. Both these methods do not discriminate between permanent and pH-dependent charges. Acid-base titrations can be used to determine surface charge-pH relationship and the soil's zero point of charge ( $\text{pH}_{\text{Zpc}}$ ) (Reed and Matsumoto 1991, Tan 1982). An example of this relationship is presented in Figure 3.4 for a colloid at several ionic strengths (James and Parks 1977). The potential and surface charge can be related by a number of models, such as, the Guoy-Chapman or Triple Layer Model (Reed and Matsumoto 1991). The zeta potential-pH relationship is measured separately by direct analytical methods and thus, it is used to verify the results of the pH-surface charge model.

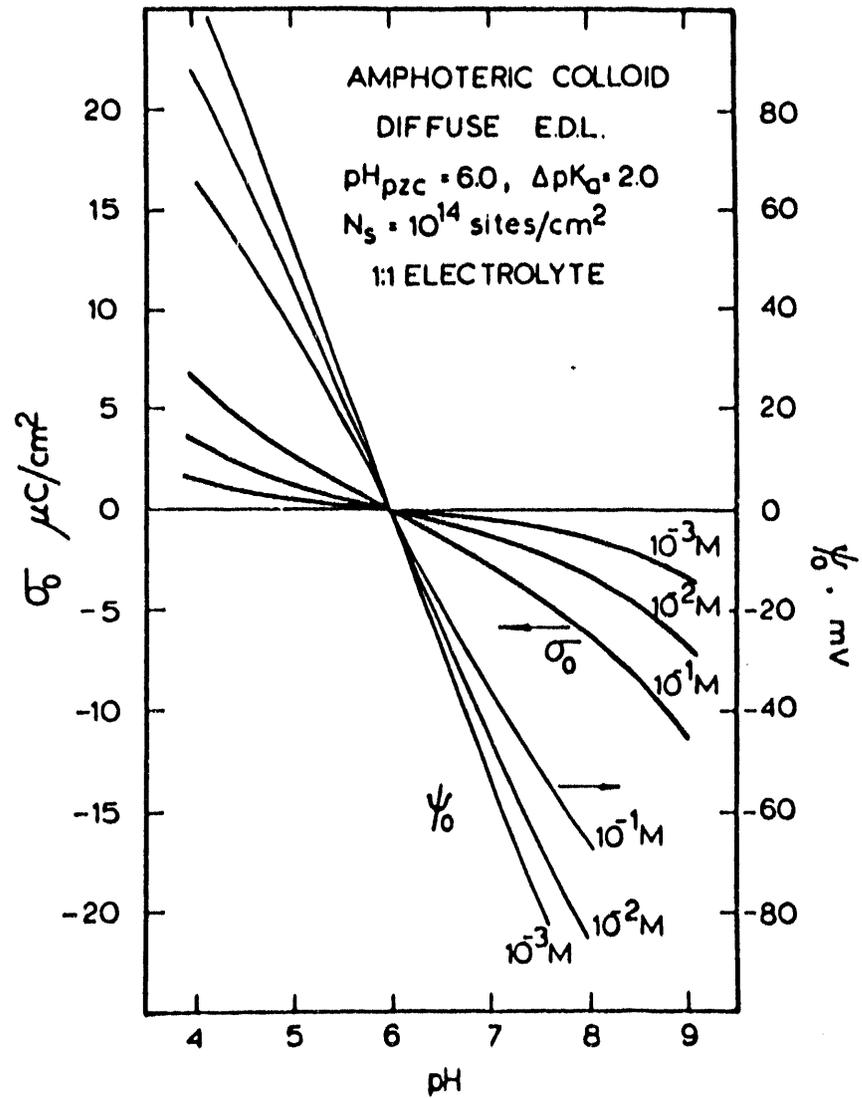


Figure 3.4. Variation of Surface Charge and Potential with pH (James and Parks 1977).

As will be discussed in greater detail later, during electrokinetics, a  $H^+$  front sweeps across the soil from the anode to the cathode. Since the EO flow is dependent on the sign and magnitude of surface charge and the characteristics of the EDL, a thorough understanding of this relationship is important in understanding the electrokinetic phenomenon. **Very little research has been conducted relating EO flow to the surface charge-pH relationship.** While Gray and Mitchell (1967) discussed at length the relationship between EO flow and surface charge, their work was conducted for short time periods and thus, a constant soil pH. Additional research is required on EO flow in a pH changing environment (the situation that would occur in the field).

### 3.1.3 Behavior of the EDL

The behavior of the EDL is a function of the surface charge, background electrolyte concentration (measured as ionic strength or conductivity), and water content. To demonstrate the relationship between the surface charge, EDL, conductivity, water content, and pH on EO flow several scenarios will be discussed. The theoretical relationship between EO flow, surface charge, water content, and electrolyte concentration is presented in Figure 3.5 (Gray and Mitchell, 1967).

**Scenario 1: Changing Ionic Strength (Conductivity).** Consider a clay soil at a constant surface charge and water content. In a system where the conductivity is low, the EDL extends relatively far out into the pore solution allowing a large concentration of co-ions and  $H_2O$  to reside in the EDL. As the conductivity of the pore liquid increases, the EDL is compressed and surface charge neutralization occurs over a smaller distance (or volume). Note, changing the conductivity does not alter the intrinsic surface charge. As the concentration of electrolyte is increased, co-ions and  $H_2O$  are "squeezed" out of the EDL. Ion exclusion is often modeled using the Donnan Exclusion Theory (1924). The exclusion of co-ions is beneficial as was discussed earlier - more counterions, more flow. However, the exclusion of  $H_2O$  is detrimental because the amount of water available to be dragged along with the migrating cation is reduced. Another way of stating this phenomenon is that the water-counterion ratio is decreased.

**Scenario 2: Changing Surface Charge.** Consider two clays at a constant conductivity and water content. The first clay has a high surface charge ("active clay") and the second has a low surface charge ("inactive clay"). The distance the EDL extends away from the surface for the active clay will be less than that of the inactive clay. The active clay has better co-ion exclusion but has a lower water-counterion ratio compared with the inactive clay. Except for very high ionic strengths, EO flow for the inactive clay will be greater than that of the active clay. Because the EDL of the active clay is always more compressed compared to the inactive clay, ionic strength changes will affect the EO flow more dramatically for the inactive clay.

**Scenario 3: Changing Water Content.** Water content is defined as the weight of water divided by the weight of soil. As the water content is decreased, the water-counterion ratio is decreased resulting in a decrease in EO flow.

**Scenario 4: Changing pH.** The effect of pH on EO flow is more difficult to generalize because as the pH changes the surface charge (magnitude and possibly the sign) and conductivity of the system will be altered. If the change in pH results in a larger surface charge and conductivity, EO

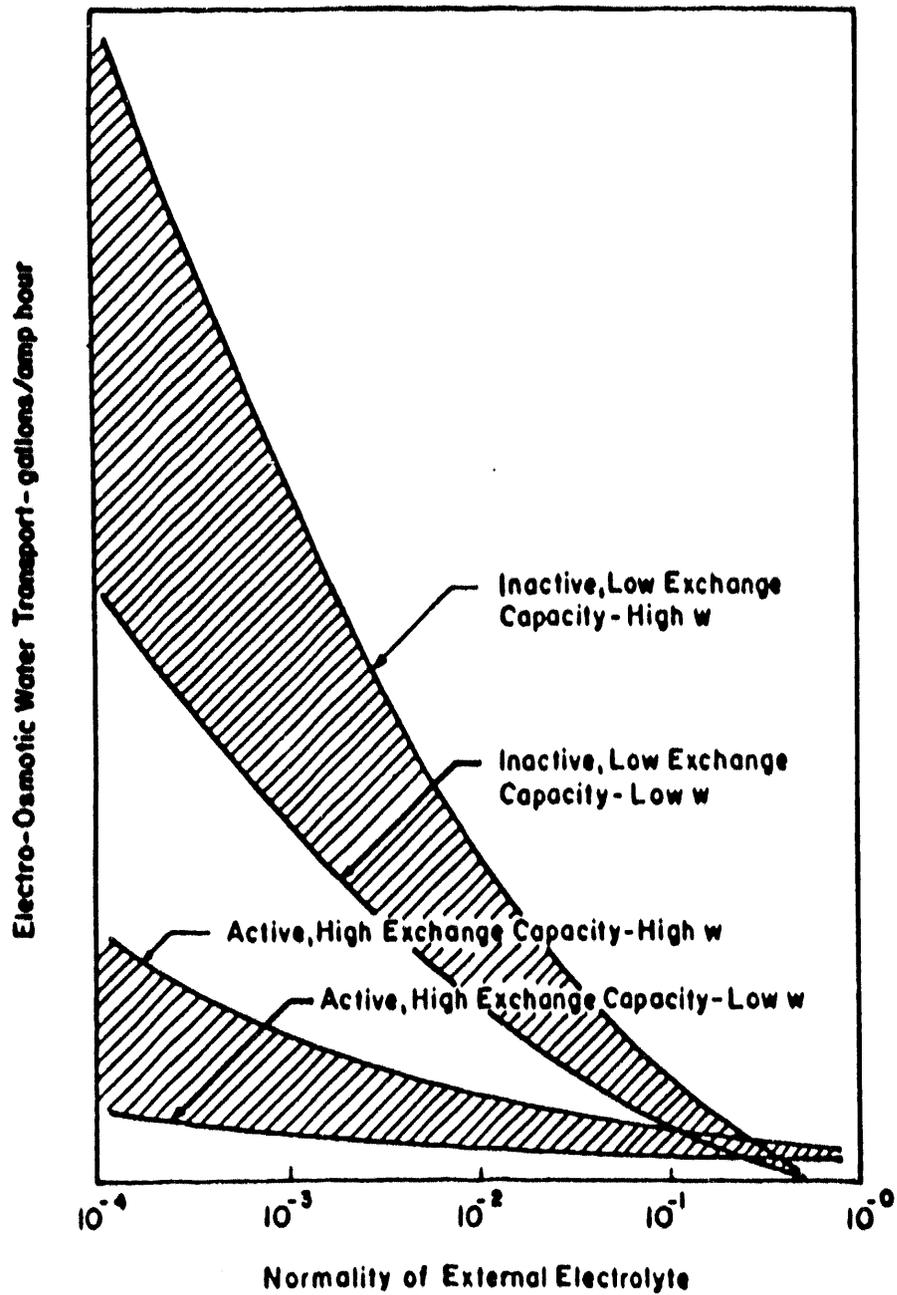


Figure 3.5. Prediction of EO Flow in Active and Inactive Clays (Gray and Mitchell 1967)

flow will decrease. As mentioned previously, the affect of pH on EO flow is important because wide variations in soil pH will occur during electrokinetic remediation.

### 3.2 MATHEMATICAL MODELING OF EO FLOW

The material presented in this section represents the initial development of a theoretical model that accounts for all phenomena occurring during the application of an applied current. Because the experimental work completed in this project focused on developing methods which improve the transport of the study contaminant, the theoretical model was not calibrated. In future work, experiments designed to ascertain model parameters, will be conducted.

The application of a direct current across saturated soils produces several simultaneous flows of fluid, ions, and electricity. The potential driving forces primarily responsible for these flows include: 1) electrical, 2) chemical, 3) hydraulic, and 4) temperature gradients across the soil (Mitchell, 1976). According to Mitchell (1991) temperature gradients in fully saturated soils are of limited influence on the movement of fluid (*i.e.*, thermo-osmosis can be neglected). Furthermore the effect of temperature gradients on both current (*i.e.*, the Seebeck effect) and ion flow (*i.e.*, the Soret effect), although not completely evaluated, are also neglected. Thus, the development of a model to predict fluid, current, and ion transport through saturated porous media induced by the direct current field includes the coupled effects of hydraulic, electrical and chemical gradients.

Assuming a homogeneous saturated porous media, the flow rate (or flux  $J$ ) of fluid, current, and ions (or complexes) produced by each gradient ( $X$ ) can be written in terms of the following set of linear equations (Mitchell and Yeung, 1991):

$$J_i = \sum_{j=1}^3 L_{ij} X_j \quad (j=1,2,3) \quad (4)$$

where  $J_j$  is the flux associated with the  $i$ th flow (fluid, current, or ion/complex),  $X_j$  is the driving force associated with the  $j$ th gradient ( $h$ =hydraulic,  $e$ =electrical, or  $c$ =chemical), the  $L_{ij}$ 's (*i.e.*,  $i=j$ ) represent the conductivity coefficients of flow, and the  $L_{ij}$ 's ( $i \neq j$ ) are called the coupled coefficients. In the case where a flow rate is produced by its associated gradient ( $i=j$ ), the flux is given by well known relationships for hydraulic flow (*i.e.*, Darcy's law), electrical flow (*i.e.*, Ohm's law), and chemical flow (*i.e.*, Fick's law). Provided that the flows of water, ions/complexes, and current do not deform and change the physical or chemical state of the porous media, the coefficients (*i.e.*,  $L_{ij}$ 's) are constants. However, in situations in which the physical or chemical state of the soil medium is effected by the fluid, current, and/or ion/complex flux, both the conductivity and coupled coefficients may vary over the time course of the electrokinetic process. The specific models for the fluxes of fluid, ions/complexes and current based on Equation 4 are discussed below.

#### 3.2.1 Fluid Flux

Based on Equation 4 the fluid flux is written as follows:

$$J_{\text{fluid}} = L_{\text{fluid,h}} X_h + L_{\text{fluid,e}} X_e + L_{\text{fluid,c}} X_c \quad (5)$$

where the terms in Equation 5 represent the flux due to hydraulic, electrical and chemical gradients respectively. The fluid flux due to chemical gradients is significant only in the presence of large chain molecules in very active clay deposits (Mitchell *et al.*, 1973). Assuming that the fluid flow induced by chemical gradients (*i.e.*, osmosis) is negligible Equation 5 can be written as follows:

$$J_{\text{fluid}} = K_h \nabla \cdot (-h) + K_e \nabla \cdot (-E) \quad (6)$$

where the first term on the right hand side of Equation 6 is Darcy's law with  $K_h$  being the hydraulic conductivity (cm/s) and  $h$  the hydraulic head (cm), and the second term representing the fluid flow induced by an electrical gradient (*i.e.*, electro-osmosis) with  $K_e$  being the electro-osmotic permeability (cm<sup>2</sup>/s per V), and  $E$  the electric potential (V).

Both parameters  $K_h$  and  $K_e$  in Equation 6 are empirical coefficients whose fundamental components are quite complex. The hydraulic conductivity ( $K_h$ ) depends on several fundamental factors such as particle and pore size distribution, and tortuosity of fluid flow paths. However, under the assumption of saturated conditions (*i.e.*, the state of the system is invariant with respect to water content) the hydraulic conductivity is fairly constant. The electro-osmotic permeability coefficient ( $K_e$ ) depends on such factors as the porosity and the electrostatic potential (*i.e.*, zeta potential) in the soil. Assuming soil pores are treated as capillary tubes,  $K_e$  can be described using the theory of Helmholtz-Smoluchowski (Hunter, 1981) given below:

$$K_e = \varepsilon \zeta n / \eta \quad (7)$$

where  $\varepsilon$  is the permittivity of the medium (farad/cm),  $\zeta$  is the zeta potential (V),  $\eta$  is the viscosity (N-sec/cm<sup>2</sup>), and  $n$  is the porosity of the medium.  $K_e$  is mainly dependent on porosity and zeta potential. Although assumed constant in most studies, data suggests that  $K_e$  varies over the time course of the electrokinetic process (Acar *et al.*, 1991; Hamed *et al.*, 1991). Figure 3.6 shows the changes in  $K_e$  over the course of the electrokinetic process in kaolinite (Hamed *et al.*, 1991). Factors that may effect  $K_e$  include pH, electrolyte concentration, and medium capacitance. These factors have a direct affect on the zeta potential and permittivity given in Equation 7.

### 3.2.2 Ion Flux

The primary driving forces for the movement of ions induced by electrokinetics are the chemical and electrical gradients along with the mass flow of fluid. Using Equation 4 the ion (or complex) flux for a given species can be written as follows:

$$J_{\text{ion}} = L_{\text{ion,c}} X_c + L_{\text{ion,e}} X_e + L_{\text{ion,h}} X_h \quad (8)$$

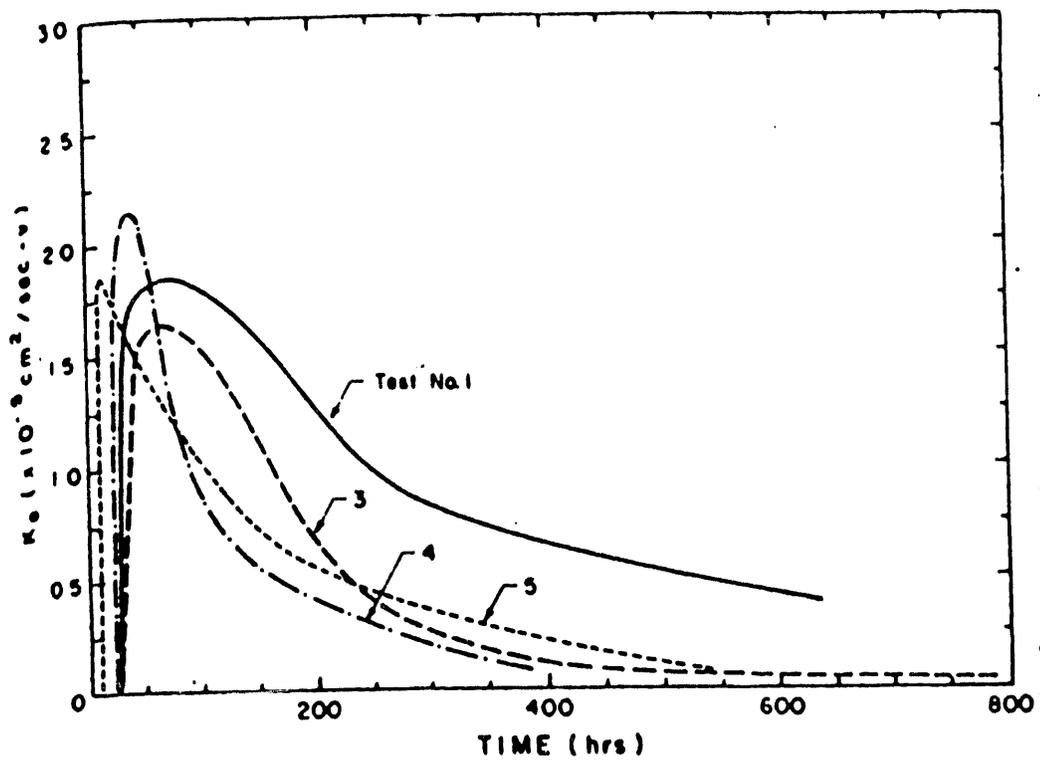


Figure 3.6. Changes in Electroosmotic Coefficient ( $K_e$ ) During the Electrokinetic Process in Kaolinite (Hamed *et al.* 1991).

The first term in Equation 8 is the ion diffusion and is given by Fick's law, the second term is the ion flux due to an electrical gradient (*i.e.*, electrolysis), and the third represents the movement due to the mass flow of fluid (*i.e.*, advection). Equation 8 can be written for a given ionic species (or complex)  $i$  as follows:

$$J_i = D_i^* \nabla \cdot (-c_i) + \left( \frac{|z_i|}{z_i} \right) c_i u_i^* \nabla \cdot (-E) + c_i J_{fluid} \quad (9)$$

where  $D_i^*$  is the effective diffusion coefficient ( $\text{cm}^2/\text{sec}$ ),  $Z_i$  is the charge of species  $i$ ,  $u_i^*$  is the effective ionic mobility of species  $i$ , and  $J_{fluid}$  is the fluid flux as given by Equation 6. The effective diffusion coefficient  $D_i^*$  is a function of the diffusion coefficient of the ionic species in free solution along with specific properties of the porous media. The effective diffusion coefficient can be empirically determined by (Bear, 1972):

$$D_i^* = D_i \tau n \quad (10)$$

where  $D_i$  is the diffusion of ion  $i$  in free solution,  $\tau$  is the tortuosity of the soil medium (*i.e.*, a measure of the complexity of flow paths), and  $n$  is the porosity of the soil. Experimental procedures to estimate the effective diffusion coefficient are necessary for each ion and soil type. The effective ionic mobility ( $u_i^*$ ) defines the velocity of an ion in soil pores due to an electric gradient. Although this parameter can not be measured directly, it can be related to the effective diffusion coefficient by the following (Mitchell, 1991):

$$u_i^* = \frac{D_i^* |z_i| F}{RT} \quad (11)$$

where  $F$  is Faraday's constant (96,485 Coulombs),  $R$  is the universal gas constant ( $8.314 \times 10^{-7}$  erg/mole deg), and  $T$  is the absolute temperature. Both the diffusion coefficient and the ionic mobility are considerably less in soil than in free solution. This is due to such factors as the tortuous flow paths, small fluid volume for flow, ion adsorption by particle surfaces, and electro-osmotic counter flow (Mitchell, 1991).

### 3.2.3 Current Flux

The current flux depends primarily on both electrical and chemical gradients. Since the current flux produced by a hydraulic gradient in fined grained soil is quite small, it is neglected. Based on Equation 4 the following equation can be written for current flux:

$$J_{current} = L_{current,e} X_e + L_{current,c} X_c \quad (12)$$

The first term on the right hand side of Equation 12 is the flux produced by an electrical gradient and given by Ohm's law, the second term is the flux produced by a chemical gradient (*i.e.*,

diffusion potential). Thus, Equation 12 can be written as follows with Equation 14 ensuring electrical neutrality:

$$J_{\text{current}} = \sigma^* \nabla \cdot (-E) + F \sum_{i=1}^N z_i D_i^* \nabla \cdot (-c_i) \quad (13)$$

$$\sum_{i=1}^N c_i z_i = 0 \quad (14)$$

where  $\sigma^*$  is the effective electrical conductivity (siemens/cm) of the free fluid in soil pores, and the diffusion potentials given by the second term on the right hand side are summed over all  $N$  ions/complexes in solution. The electrical conductivity  $\sigma^*$  is a function of the ionic mobility of all species and is given by Equation 15 (Alshawabkeh and Acar, 1991). Note that the conductivity is defined over the species in solution and not in the electric double layer (*i.e.*, neglecting surface conductivity).

$$\sigma^* = F \sum_{i=1}^N |z_i| c_i u_i^* \quad (15)$$

### 3.2.4 Conservation of Mass and Charge

To model the transport of fluid, ions (or complexes) and current, time dependent conservation of mass and charge equations are written utilizing the fluxes derived above for fluid, ions, and current. A mass balance differential equation for fluid and ions (and complexes) is given as follows:

$$\frac{\partial(\rho_{\text{fluid}} \theta)}{\partial t} = -\nabla \cdot J_{\text{fluid}} \quad (16)$$

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i + nR_j \quad (17)$$

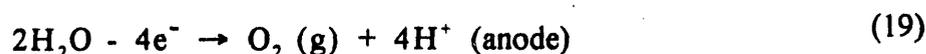
where  $\rho_{\text{fluid}}$  and  $\theta$  are the fluid density ( $\text{g/cm}^3$ ) and the volumetric water content ( $\text{cm}^3$ ) respectively, the left hand side of Equation 17 is the time rate of change of the concentration of the  $i$ th aqueous ion (or complex), the first term on the right hand side represents the flux gradients of each species, and  $R_j$  denotes a set of  $j$  rates of removal/production of the  $i$ th ion (or complex). The flux derived for ions (or complexes) is given by Equation 9 which combines the contributions from electrical and chemical gradients along with the mass flow of fluid (*i.e.*, advection). The removal/production rates  $R_j$  typically have several components including sorption (adsorption, chemi-sorption, and ion exchange), aqueous phase reactions, and precipitation/dissolution reactions. Several models exist to predict ion sorption (*e.g.*, equilibrium and Langmuir isotherms), aqueous phase reactions, and precipitation/dissolution reactions. (See both Travis and Etnier (1981) and Sposito (1984) for excellent reviews of reaction models).

A conservation of charge differential equation can also be written as follows (Alshawabkeh and Acar, 1991):

$$\frac{dV}{dt} = -\nabla \cdot J_{\text{current}} \quad (18)$$

where  $V$  is the volumetric charge density of the soil ( $C/cm^3$ ) with the current flux in the above equation given by Equation 13.

The simultaneous solution of the time dependent differential equations given by Equations 16-18 yields a prediction for the fluid, ion (or complex), and current transport across a saturated soil under an applied direct current. Boundary conditions for this electrokinetic process assuming inert electrodes and 100% faradaic efficiency in a saturated soil yields the following at both the cathode and anode (Hamed *et al.*, 1991):



Note that the production of  $H^+$  ions at the anode decreases the pH while the production of  $OH^-$  ions at the cathode increases pH.

### 3.2.5 Summary of Models Found in Literature

Several models of fluid, ion (or complex), and current flow based on a mass balance approach are found in literature. An excellent review of such models is found in Alshawabkeh and Acar (1991). Early models of electrokinetics involved the prediction of electro-osmotic consolidation of clays (*e.g.*, Ersig, 1968; Lewis and Humpheson, 1973). These models assumed a constant electrical gradient across the soil and neglected the chemistry associated with the electrokinetic process (*i.e.*, surface chemistry). The focus of these models was the assessment of water removal for consolidation purposes.

As researchers began to examine the use of electrokinetics as a means to remediate contaminated soils, more emphasis was given to the prediction of ion (and complex) flow. Acar *et al.* (1991) developed a one-dimensional model to predict the migration of the pH front from the anode to the cathode. The model included hydraulic, chemical and electrical gradients. However, it was assumed that these gradients were constant in time and space. Model results were reasonable good (although comparison of model results to predictions on a log scale tends to hide the sensitivity of model error). Mitchell and Yeung (1991) developed a model of the behavior of ions in soil under a direct current. In this case they were interested in the use of electrokinetics as a barrier; *i.e.*, to stop the migration of pollutants. The ions (or contaminants) of interest were sodium ( $Na^+$ ) and chloride ( $Cl^-$ ). A one-dimensional model was developed that included hydraulic, chemical and electrical gradients. However, it was also assumed that the hydraulic and electrical potentials were constant over the time course of the electrokinetic process.

Furthermore, the chemistry associated with the electrodes (*i.e.*, the production of an acid front) was not included. Model results did however capture the gross behavior of experimental results. More recently Shapiro and Probst (1993) developed a one-dimensional model to predict the transport of phenol and acetic acid in saturated clay. The contribution of this model is the inclusion of a chemical adsorption equilibrium isotherm (although precipitation dissolution reactions are not included), and the inclusion of local solution pH on surface charge. This model, however, neglects the coupling between hydraulic and electrical potentials in ion transport. A comparison between model predictions and experimental data for two experiments involving the transport of acetic acid is given in Figure 3.7 (Shapiro and Probst 1993). Results appear to accurately predict the removal of acetic acid early on in the experiment whereas deviations between model predictions and experimental results widen as the experiment continues.

Major limitations exist in the current modeling approaches. Of primary importance is the inclusion of the effect of electrokinetics on the chemical state and properties of the soil fluid medium. Current models assume that the chemical state of the medium remains constant over the time course of the EK process. However, as the pH front moves across the soil, changes in surface chemistry induces potential changes in local zeta potentials, conductivity (due to changes in ionic strength), capacitance, and potential speciation of contaminants. These changes in turn may effect electrical and chemical gradients in local areas. Current models do not capture these coupled effects caused by such complex chemical behavior resulting in inadequate predictions.

### **3.3 CHEMICAL REACTIONS ASSOCIATED WITH EK**

Chemical reactions important in EK are divided into two classes; those that occur because of the electric field and those that would occur in the absence of the applied electric field. For convenience, each class of reactions are discussed separately in the next sections.

#### **3.3.1 Reactions in the Absence of An Electric Field**

Examples of reactions that would occur in the absence of an electric field include adsorption-desorption of the contaminant from soil surfaces, precipitation-dissolution reactions, and interactions between soluble chemical constituents in the pore water. For most inorganic contaminants, the pH of the soil system is a critical parameter. For cationic metals, increasing the pH increases the amount of metal removed by adsorption and surface precipitation. An example of this phenomenon is presented in Figure 3.8 for lead and an actual soil (Cline and Reed, 1993). The curves in Figure 3.8 are referred to as "pH-adsorption edges". As the pH increases the amount of lead removed by the soil increases. If the pH is lowered by the addition of an acid, lead will desorb from the soil. This desorption-pH relationship is used in soil washing technology and as will be discussed in the next section is an important phenomenon in EK soil remediation. In Figure 3.9, pH-adsorption edges for several heavy metals and a silt clay loam are presented (Elliot *et al.* 1986). Note that sorption behavior is dramatically different between metals.

Interactions between soluble chemical constituents are often referred to as complexation reactions and usually depend on pH. The simplest (and ubiquitous) reactions are between the contaminant and OH. In Figure 3.10, the lead solubility diagram for hydroxide species is presented (Cline

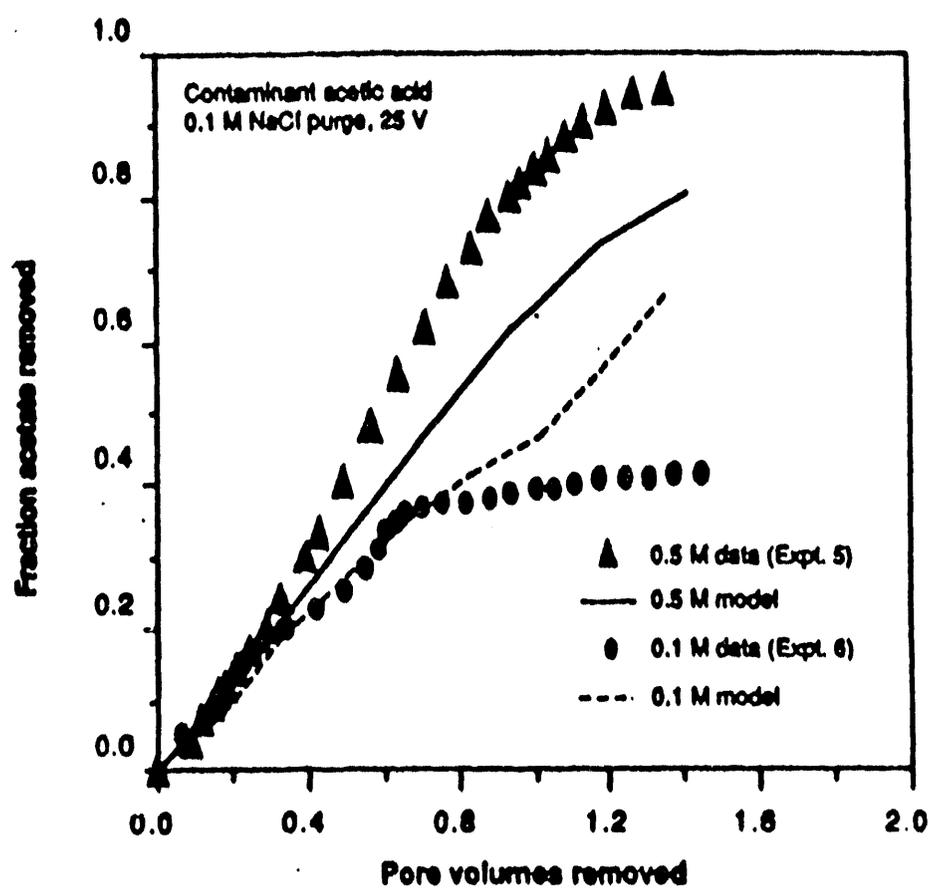


Figure 3.7. Fraction of Acetate Removed vs Pore Volumes For a Sigma Clay Using a 0.1 M NaCl Purge; Comparison of Model Predictions and Experimental Results (Shapiro and Probstein 1993).

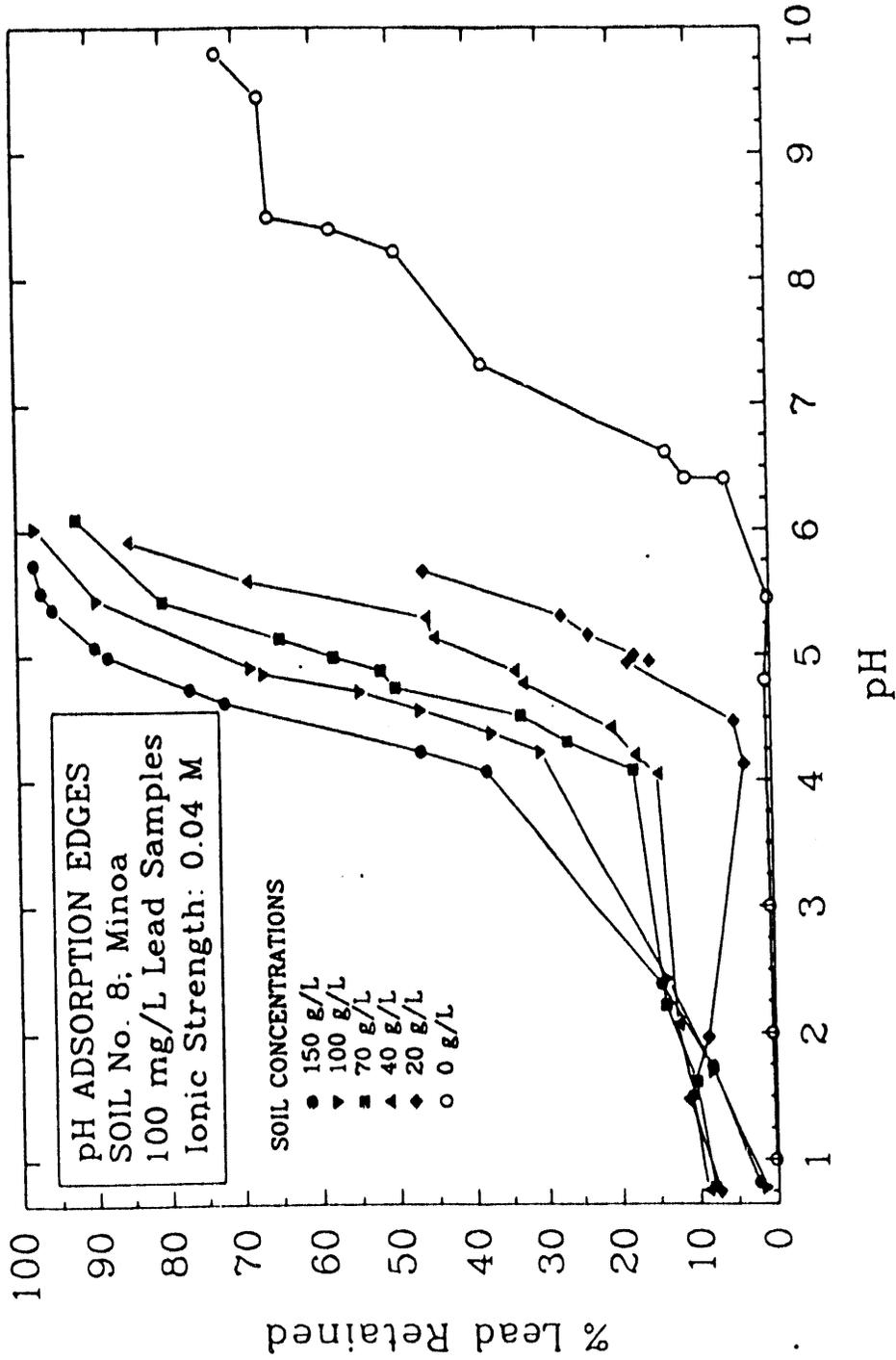


Figure 3.8. Lead pH-Adsorption Edges for a Minoa Silt Loam.

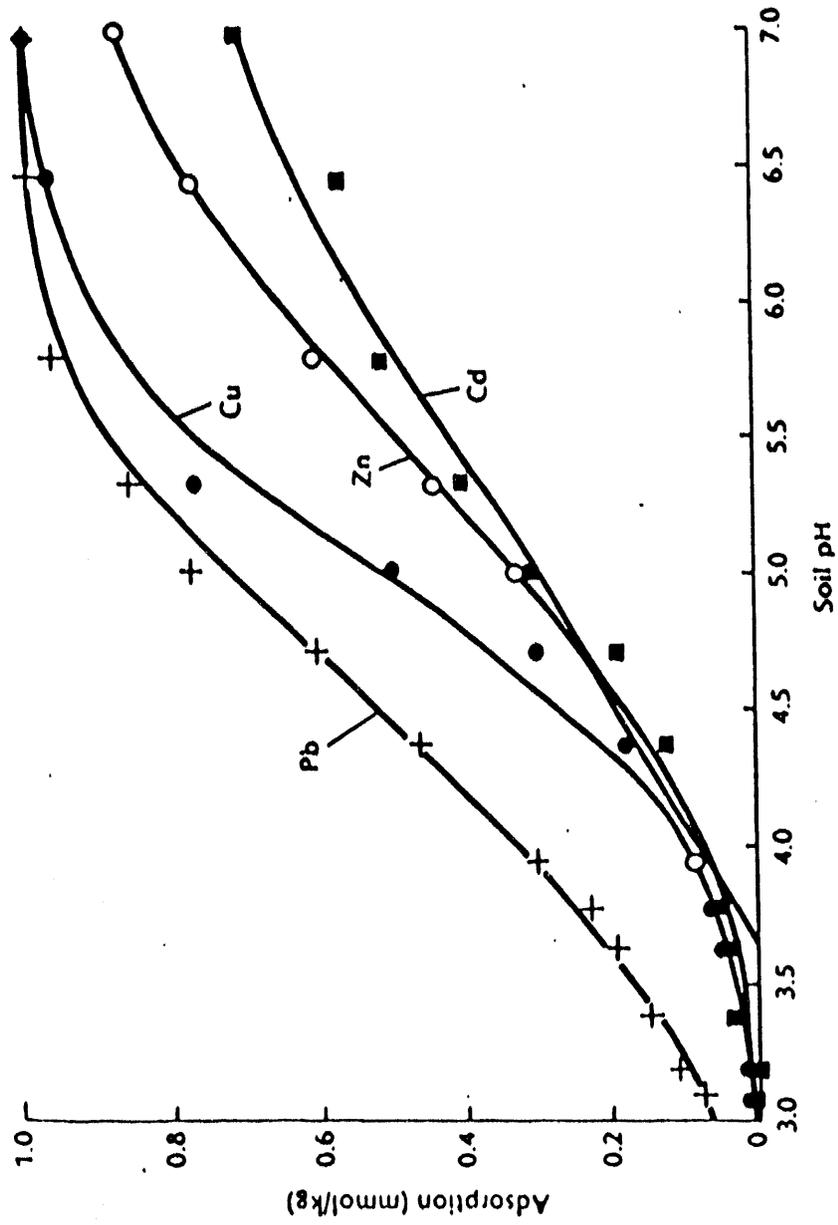


Figure 3.9. pH-Adsorption Edges for Several Heavy Metals on a Silty Clay Loam (Elliott *et al.* 1986).

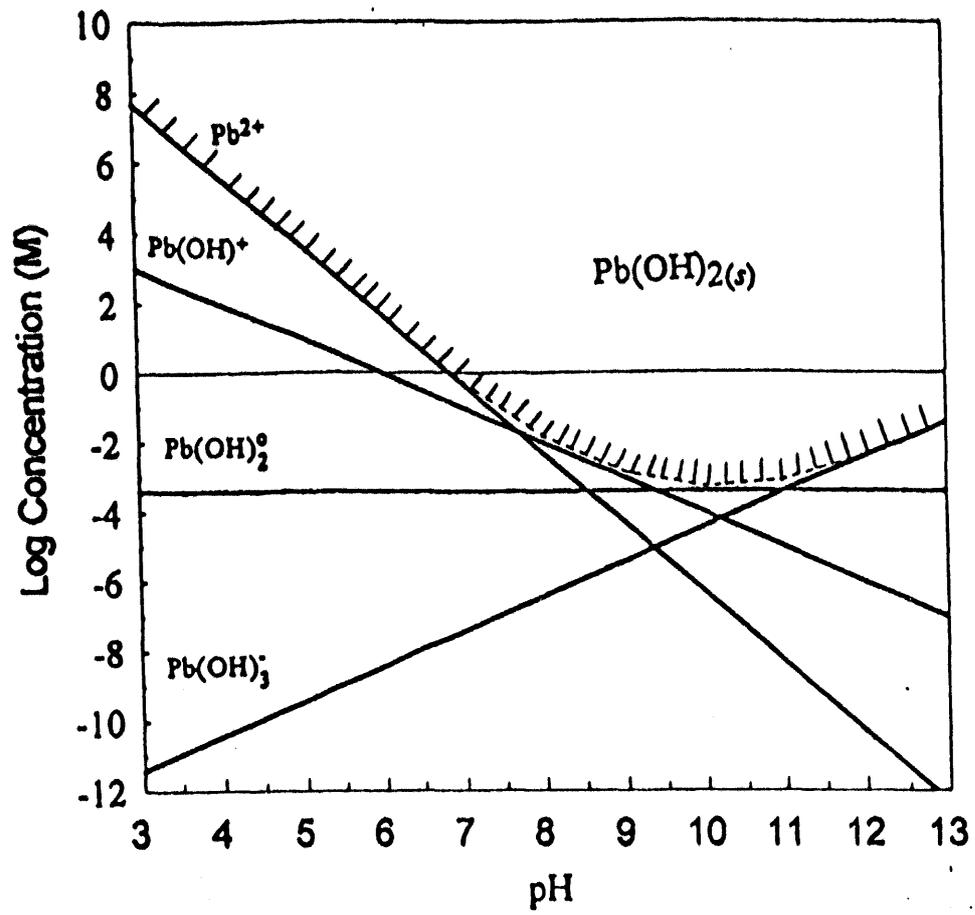
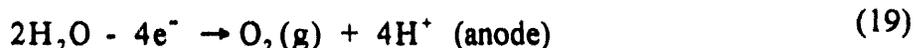


Figure 3.10. Lead Hydroxide Solubility Diagram.

1993). In soil systems other constituents are present, such as carbonate, making the chemical speciation more complex. The lead solubility diagram for carbonate and hydroxide species is presented in Figure 3.11. The form of lead (either aqueous species or solid) is a function of pH. The complexity of the system increases as the number of complexing species is increased. While it is not possible to calculate a sorption/speciation/solubility relationship that completely describes contaminant chemistry in a soil, the diagrams in Figures 3.8 through 3.11 are helpful in understanding the general behavior of the contaminant during EK flushing.

### 3.3.2 Electric Field Produced Reactions

Electric field produced reactions can be divided into electrodic and electrochemical reactions. Electrodic reactions are defined as the reactions between the contaminant and the electrode. Examples of electrodic reactions are the "plating" of a heavy metal on the cathode and the electrolysis of water at both electrodes. Plating on the cathode can be avoided by the proper selection of electrode material. Electrochemical reactions refer to the reactions that result from the electron transfer (oxidation-reduction) and from the separation of ions in the electrolyte under an applied electric field (electrolytic migration). Of these reactions, the most important are electrolytic migration and the electrolysis of water in the electrode reservoirs. As was discussed earlier, electrolytic migration is the movement of ions towards the electrode of opposite charge. The water electrolysis reactions are defined by Equations 19 and 20 (repeated here for convenience)



These reactions are the primary reason for changes in the soil system chemistry during electrokinetics. An example of how the soil pH changes during EK is presented in Figure 3.12 (results from testing of the EK reactors). The top graph in Figure 3.12 is the pH profile before the application of an applied current (30 V) and the bottom graph is pH profile after several days of EK flushing.  $\text{H}^+$  that were produced at the anode were swept toward the cathode with the electroosmotic movement of water producing an acidic front. The cathode reaction produced  $\text{OH}^-$ , which diffused into the soil against the flow of water. A zone of high pH near the cathode resulted. The pH changes that occur during EK flushing affect the electroosmotic flow (through the change in surface charge, conductivity, *etc.*) as well as the sorption/speciation/solubility of the contaminant (see Figures 3.8 through 3.11). Specifically, the low pH front generated at the anode causes desorption and ionization of most cationic heavy metals while the high pH zone produced at the cathode causes precipitation of the migrating heavy metals, preventing their movement into the cathode reservoir. A focus of this research was the development of methods to lower the cathode reservoir pH so that the migrating heavy metals will not precipitate in the soil. For cations that do not form solids (*e.g.*, Sr, Cs) the high pH only reduces the extent of desorption from the soil. For most anionic inorganic contaminants, desorption decreases with decreasing pH thus, the opposite behavior would occur. For nonionic organic contaminants, pH is not usually critical to the sorption phenomenon.

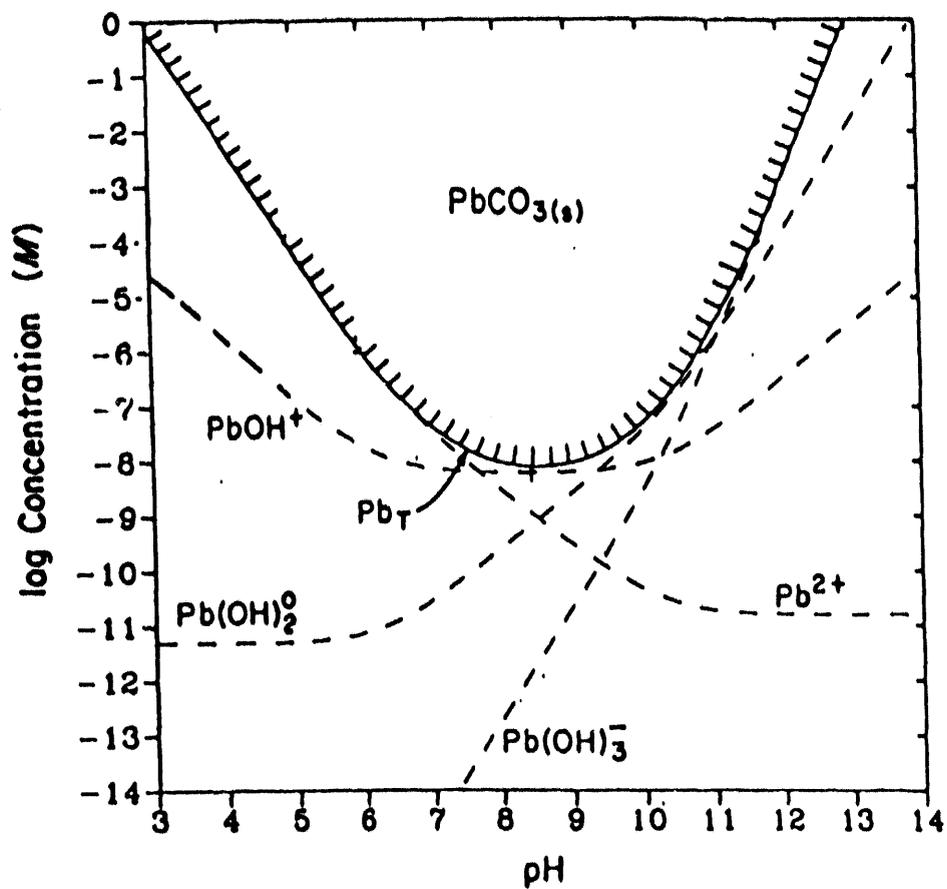


Figure 3.11. Lead Carbonate Solubility Diagram.

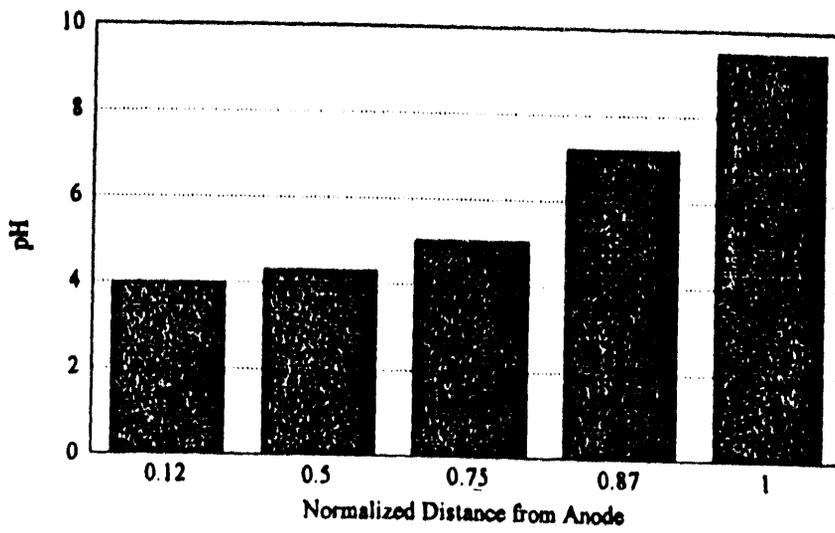
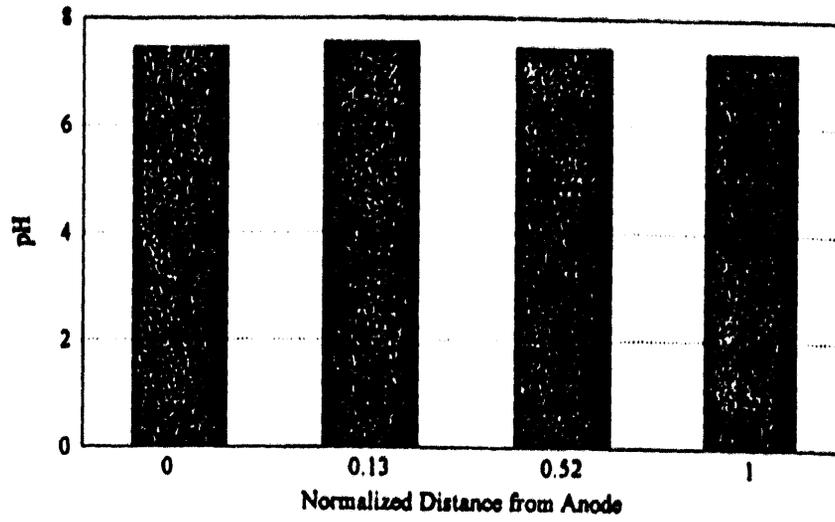


Figure 3.12. Soil pH Profiles Before (Top) and After (Bottom) EK Flushing.

### 3.4 SUMMARY OF EK RESEARCH

While electroosmosis has been used in the field for decades, electrokinetic remediation of contaminated soils is a relatively new technology. For the readers convenience, a list of recent published work relevant to EK research efforts is presented in Table 1 in chronological order. Based on the data listed in Table 3.1 it is apparent that electrokinetic remediation is a new technology with a limited number of researchers working in this area. In the future, the amount of published work and the number of researchers working on the problem should increase dramatically. In the next several paragraphs, several of the studies listed in Table 3.1 having to do with the decontamination aspect of EK will be discussed in greater detail. In addition, recent work by the authors will be presented.

**Table 3.1. Summary of Recent Published EK Research Efforts**

Author(s)	Year	Research Description
Gray and Mitchell	1967	Electroosmotic water movement in illite and kaolinite.
Segall, <i>et al.</i>	1980	Water quality resulting from EO application to uncontaminated soils.
Lockhart	1983	Electroosmotic dewatering of kaolinite.
Casagrande	1983	Investigation of EO water movement in uncontaminated soils..
Horng, <i>et al.</i>	1987	Lab-scale testing of chrome removal from the "Chrome Products Site" in Corvallis, Oregon.
Acar, <i>et al.</i>	1991	Investigation of pH distribution that occurs in a soil (kaolinite) during EO/EK.
Lagemen	1989	Summary of field-scale work performed by <i>Geokinetics</i> (Rotterdam, The Netherlands).
Bruell, <i>et al.</i>	1990	Removal of gasoline hydrocarbon and TCE from kaolinite
Cabrera-Guzman, Swartzbaugh, <i>et al.</i>	1990	Summary of EPA sponsored (SITE Program) assessment of EK technology.
Hamed <i>et al.</i>	1991	Removal of Pb (~100 mg/kg) from a pure, saturated kaolinite.
Korfiatis, <i>et al.</i>	1991	Investigation of combined EO and hydraulically induced flow in kaolinite.
Mitchell and Yeung	1991	Use of EO/EK as a flow barrier in compacted clays ("EK fencing").
Mitchell	1991	Description of Coupled Flows (hydraulic, electric, thermal, chemical) in soils ("Rankine Lecture").
Pamukcu, <i>et al.</i>	1991	Zinc removal from kaolinite.
Acar, <i>et al.</i>	1992	Removal of phenol from kaolinite.
Alshawabkeh and Acar	1992	Review of the parameters affecting EK remediation.
Dahab, <i>et al.</i>	1992	Removal of Cu in an unsaturated silica sand.

**Table 3.1. Summary of Recent Published EK Research Efforts, continued**

Kelsh	1992	Cs removal from soils from the Chernobyl site.
Pamukcu and Wittle	1992	Removal of heavy metals from kaolinite, montmorillonite, and sand mixtures
Pamukcu and Wittle	1992	Removal of low-level radioactivity radionuclides from kaolinite, montmorillonite, and sand mixtures.
Segall and Bruell	1992	Transport of nutrients (N, P) under EO. Potential use in <i>in-situ</i> bioremediation.
Triay <i>et al.</i>	1992	Removal of actinides (Pu, Am, U) with the aid of complexing agents.
Hatfield, <i>et al.</i>	1993	Removal of Pb from an actual fine-grained soil (Authors' DOE sponsored work).
Shapiro and Probst	1993	Removal of phenol and acetic acid from kaolinite.

Pamukcu and Wittle (DOE report presently under agency review) conducted an extensive study on the use of EK for the remediation of several synthetic clay mixtures contaminated with heavy metals (Cd, Hg, Pb, Ni, Zn), nonradioactive radionuclides (Co, Cs, Sr, U), anions ( $\text{HAsO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ), and hydrocarbons (chlorobenzene, hexachlorobenzene, phenol, TCE, acetic acid, acetone). Their research was sponsored by the DOE's Office of Research and Development. The majority of their EK flushing experiments were short-term in nature (24-48 hours) and were used to answer the question "can a contaminant be transported via EK?". Because of the short duration of the experiments, the majority of the contaminants still resided in the soil as a whole, but were concentrated in the portion of the soil nearest the electrode of opposite charge. For example, the concentration of a cationic heavy metal near the anode was less than the initial concentration, but was higher than the initial near the cathode. Up to 99 percent of the cationic contaminants were removed from portions of the soil near the anode. Cations less likely to form precipitants (*e.g.*, zinc) were more likely to be removed. For organic contaminants that were poorly adsorbed and existed in a nonionized state, migration was solely due to electroosmotic flow.

Pb removal from kaolinite was investigated Hamed *et al.* (1991). Pb was selected because of its widespread presence at hazardous waste sites. Soil Pb concentrations between 118 and 145 mg/kg were employed. The soil-water-contaminant specimen was consolidated at a maximum pressure of 29 psi. The specimen water content after consolidation varied from 65% at the ends to 92% in the center, due to incomplete consolidation. A constant current (1 to 3 mA) was applied in all tests to keep the net rate of electrolysis constant. The cross-sectional area of the specimens was 81.1 cm<sup>2</sup>, while the specimen length was either 10.2 cm or 20.3 cm. Inert graphite electrodes were used to prevent corrosion and introduction of corrosion products. Electrolysis generated gas was released via holes at the top of each electrode reservoir. Test duration varied from 100-700 hours of applied current. There was no measurable fluid flow during the initial 10-20 hours of current application. Thereafter, the flow rate increased rapidly

and then decreased nonlinearly after approximately 300 hours of applied current. Typical average fluid flow rates were 2 - 3 mL/hr from initial current application until completion of test. The study revealed that in tests of shorter duration, the acid front was not given sufficient time to advance across the cell and lead removal was incomplete. In these tests, lead was only partially removed from the anode section and accumulated in the cathode end. In longer tests where the acid front was allowed to advance across the entire soil cell, removal ranged from 75-95% across the entire cell. As was previously discussed, the  $H^+$  produced during the electrolysis of the anode water is swept across the specimen, lowering the pH and promoting desorption of cationic contaminants. The pH in the cathode reservoir immediately rose from pH 4.0 to values around 11.0-12.0 after current application because of the  $OH^-$  produced in the cathode chamber. After about one pore volume of flow, the cathode pH dropped to between pH 5 and 6. The decrease in cathode pH was accompanied by a decrease in fluid flow rate, even though a constant electric current was maintained (Note: the opposite was observed in the authors' study). The anode reservoir pH did not exhibit a large fluctuation - initial pH 3.6 vs. pH 2.7 after test completion. The conductivity decreased in the cathode portion of the soil specimen and a net increase in soil resistance to electric current flow was observed. A proportional rise in voltage was needed to maintain a constant current. Results from this study are an example of the complexity of the EK phenomenon and point out the need for basic research into the relationship between flow, pH, conductivity, and current.

Zinc detoxification of a saturated Georgia kaolinite clay was investigated by Pamukcu *et al.* (1991). Water content of the soil averaged 58 percent after consolidation. Initial anode and cathode reservoir pH averaged 5.7. The reservoir waters were either distilled water or conditioned with NaCl and  $NH_4OH$ . For the majority of the test, a constant voltage of 30 V was applied, although higher voltages were investigated. The duration of the tests varied between 2 and 4 hours. Zn concentration within the soil samples was not measured but was monitored in the reservoir waters. At the end of the tests, Zn in the cathode reservoir was twice its initial concentration and was three times its initial concentration at the anode. The high zinc concentration at the anode was attributed to a portion of the zinc existing as  $Zn(OH)_3^-$ . Increased fluid flow was observed when NaCl was injected in the anode chamber and flow was increased further when NaCl was injected in both reservoir chambers. EO flow increased with increased voltage until about 70 V, after which it decreased.

Horng *et al.* (1987), investigated the removal of chromium under both hydraulic leaching and electrokinetics. Soil from the United Chrome Superfund Site in Corvallis, OR was used. Hydraulic leaching combined with electrokinetics reduced the time to obtain a 95 percent reduction in soil chromium concentration. The volume of contaminated water requiring further treatment was also decreased by about 50 percent compared to the hydraulic only system. This would result in a substantial decrease in the volume of contaminated water to treat after soil remediation. Cabrera-Guzman *et al.* (1990) reported on results from the firm *Geokinetics* in applying electrokinetics to actual field situations. *Geokinetics* employs chemical conditioning agents at both electrodes to optimize contaminant removal. The type of conditioning agents employed are dependent on the contaminant(s), soil type, pH, and conductivity. As was mentioned previously, for proprietary reasons, *Geokinetics* has not published specifics on their conditioning scheme. A summary of results from *Geokinetics'* studies on actual soils is presented

in Table 3.2. A fine sand and a dredged river mud were investigated. Based on the results listed in Table 3.2, some general observations can be made. Firstly, EK flushing appears to be more effective for cations than anions (Hg, As, Cr) because anions migrate towards the anode in the direction opposite of water flow. Secondly, contaminants that forms solids at higher pHs are more likely to be removed. For example, cadmium precipitates at about pH = 8 and lead precipitates at pH = 6. Lead migration is more dependent on the H<sup>+</sup> front than is cadmium (*i.e.*, a longer time will be required for lead removal). Thirdly, the percent removal decreases as the initial contaminant concentration is decreased. At lower contaminant concentrations, the average binding energy between the soil and the contaminant is higher than that at higher contamination levels. Thus, it is harder to remove the contaminant from the soil when present at low concentrations. (Cline and Reed 1993).

**Table 3.2 Summary of EK Results from Studies Conducted by *Geokinetics***

<b>SOIL TYPE: Fine Argillaceous Sand</b>			
<b>Metal</b>	<b>Initial Conc., (mg/kg)</b>	<b>Final Conc., (mg/kg)</b>	<b>Decrease, (%)</b>
Cd	319	<1	99
Cr	221	20	91
Ni	227	34	85
Pb	638	230	64
Hg	334	110	67
Cu	570	50	91
Zn	937	180	81
<b>SOIL TYPE: Dredged River Mud</b>			
Cd	10	5	50
Cu	143	41	71
Pb	173	80	54
Ni	56	5	91
Zn	901	54	94
Cr	72	26	64
Hg	0.5	0.2	60
As	13	4.4	66

Electrokinetic flushing has also been demonstrated to be effective in the remediation of soils contaminated with radionuclides. Kelsh (1992) reported that 93 percent of cesium from the 1986 Chernobyl disaster was removed from a clay soil. Less success was reported for moderately permeable soils (loamy, peat humus). Triay *et al.* (1992) documented the successful removal of actinides (Pu, Am, U) from soils and groundwaters. This study combined electrokinetics with various complexing agents to increase actinide removal. The most effective complexing agent utilized in this research was EDTA, with removals up to 100 percent.

The majority of researchers agree that electrokinetics is best suited for charged contaminants, and the literature presented so far reflects that observation. However, for completeness, a brief

literature review will be presented on the use of EK for the remediation of soil contaminated with organics. Acar *et al.* (1992) demonstrated successful electrokinetic removal of phenol from kaolinite in the laboratory. Under the influence of electroosmotic fluid flow coupled with the desorbing action of the acid front, soil-bound phenol was reduced between 85 to 95 percent. The initial concentration of phenol was 500 mg/kg. At this concentration level, most of the phenol was adsorbed by the kaolinite. A constant current of 0.316 mA was applied, which equated to a current density of 0.037 mA/cm<sup>2</sup>. Bruell *et al.* (1992) investigated the use of EK for the removal of gasoline hydrocarbons and TCE from kaolinite. Electroosmotic water flow was the primary hydrocarbon removal mechanism (*i.e.*, removal was not dependent on the movement of the acid front). Thus, hydrocarbons with relatively high water solubilities and correspondingly low distribution coefficients are readily transported/removed.

The authors of this research report took a different approach compared to the majority of the research cited above in that a single actual soil (that was synthetically contaminated) was used and the flushing experiments were of much longer durations. The use of an actual soil was based on recommendations from the "Proceedings of the Electrokinetic Workshop (DOE, 1992)". To date, the vast majority of EK research has been on "pure clays" or mixtures of commercially obtained clays and sands (*e.g.*, kaolinite, illite, *etc.*). Using these relatively homogenous materials does not necessarily mimic the field-performance of EK flushing. Long durations were also employed so that changes in soil pH could be observed and the movement of the contaminant into the reservoir waters could be realized (*i.e.*, the entire soil is remediated). Experimental methodology and results from the authors' work will be presented in the next chapter.

## 4. METHODOLOGY

In this section the methodologies used in soil selection and characterization, contamination of the study soil with lead, lead desorption experiments, the construction and testing of the electrokinetic reactors, and the remediation of lead-contaminated soil via electrokinetics are described. For the reader's convenience, the methodology used for each task is described separately.

### 4.1 SOIL SECTION AND CHARACTERIZATION

Soil was collected at a depth of three feet from an exposed bank of Tonawanda Creek, located in northern Erie County, New York. Soil was then air-dried at the West Virginia University Department of Civil Engineering's Environmental Laboratories and stored in air tight containers for future use. The soil underwent the physical and chemical characterization procedures listed in Table 4.1. Standardized test methods were employed for all characterizations except for the soil acid-base titrations.

**Table 4.1. Soil Chemical/Physical Characterizations and Methods Used**

Particle Size Analysis (ASTM Method D422)
Hydraulic Conductivity (ASTM Method D5084)
Field Moisture Content (ASTM Method D2216)
Cation Exchange Capacity (USEPA Method 9081)
Organic Matter Content (ASTM D2974)
Soil Digestion for Lead (USEPA Method 3050)
Aqueous Lead Determination (USEPA Method 7420)
Acid-Base Titrations
Soil pH (USEPA Method 9045)
Acid-Base Titrations

### 4.2 SOIL CONTAMINATION AND DESORPTION EXPERIMENTS

#### 4.2.1 Soil Contamination

The study soil was artificially contaminated with lead using aqueous lead concentrations of 10, 100, and 1000 mg/L. If 100 percent of the lead was adsorbed by the soil, soil lead concentrations would be 100, 1000, and 10000 mg/kg Pb for 10, 100, and 1000 mg/L Pb, respectively. A 10:1 solution:soil mass ratio was employed in the contamination step. Lead nitrate was the source of lead. Sodium nitrate was also added such that the final NaNO<sub>3</sub> concentration was 3200 mg/L. This value corresponds to a Total Dissolved Solids (TDS) concentration of 2300 mg/L, which is typical for groundwaters.

One hundred fifty grams of air-dried soil was sieved using a No. 10 sieve and placed in a 2 liter Nalgene container with 1.5 liters of the appropriate Pb-NaNO<sub>3</sub> solution. An aliquot of the Pb-

NaNO<sub>3</sub> solution was acidified and kept for Pb analysis. Initial slurry pH's were taken, and the samples were placed on mechanical shakers for 21 days. To reduce the possibility of lead precipitation as Pb(OH)<sub>2</sub> (s), the 1000 mg/L Pb contamination solution was pH adjusted to 4.8 with concentrated HNO<sub>3</sub> before being mixed with the soil. After 21 days, the samples were allowed to settle overnight to provide adequate time for the colloidal clay particles to settle. The supernatant was decanted and the volume removed is recorded for subsequent mass balance calculations. A small aliquot of the supernatant was filtered through a 0.45 μm filter, acidified, and analyzed for Pb content. The soil was allowed to air-dry. The difference between the Pb concentrations of the initial Pb-NaNO<sub>3</sub> solution and supernatant was used to determine the amount of soil-bound lead (*i.e.*, mass balance approach). To verify the mass balance calculations, triplicate samples of the contaminated soil underwent EPA Method 3050 Total Metal Digestions. Since indigenous Pb values were small relative to the levels of contamination used, the total Pb concentration obtained by the digestion method should be very similar to the value obtained using the mass balance approach.

#### 4.2.2 Desorption Experiments

Following the contamination step, the soil was air-dried, crushed, and passed through an ASTM number 10 sieve. In order to assess the behavior of soil-bound lead under electrokinetic conditions, the contaminated soil was extracted with the following solutions: HCl (1 and 0.1 N), HNO<sub>3</sub> (1 and 0.1 N), acetic acid (1 and 0.1 N), EDTA (0.1 and 0.01 M), and CaCl<sub>2</sub> (1 and 0.1 M). Several of the reagents were added to the electrode reservoir waters as conditioning agents.

Acids were employed to simulate the conditions that occur as the pH-front moves from the anode to the cathode. CaCl<sub>2</sub> was used to replicate the behavior of soil-bound lead as the conductivity of the pore water solution is increased. EDTA, a strong complexing agent, was used to assess its possible use as a desorptive additive to the EK process. Tap water was used to provide a benchmark.

In the batch desorption experiments, 25 mL of extraction solution was delivered (via a wide-mouth volumetric pipette) into 60 mL Nalgene bottle containing 1.00±02 grams of contaminated soil. To induce rapid equilibration, the samples were placed on mechanical shakers for a 24 hour period. At the end of the 24 hour period, the pH of the sample slurries were measured and recorded. Samples were filtered through a 0.45 μm filter, acidified with concentrated HNO<sub>3</sub> to pH < 2 if required, and stored for lead determination. Aqueous lead content was determined using USEPA Method 7420. Desorption experiments were performed in triplicate. The filter assembly was rinsed between triplicates in order to reduce the possibility of sample contamination.

### 4.3 EXPERIMENTAL APPARATUS CONSTRUCTION AND TESTING

#### 4.3.1 Apparatus Construction

The experimental apparatus consisted of a consolidation unit and electrokinetic (EK) soil reactor. Schematic of the experimental setup is presented in Figure 4.1. Detailed drawings of the consolidator and EK reactor are provided in Figures 4.2 and 4.3, respectively. A total of six

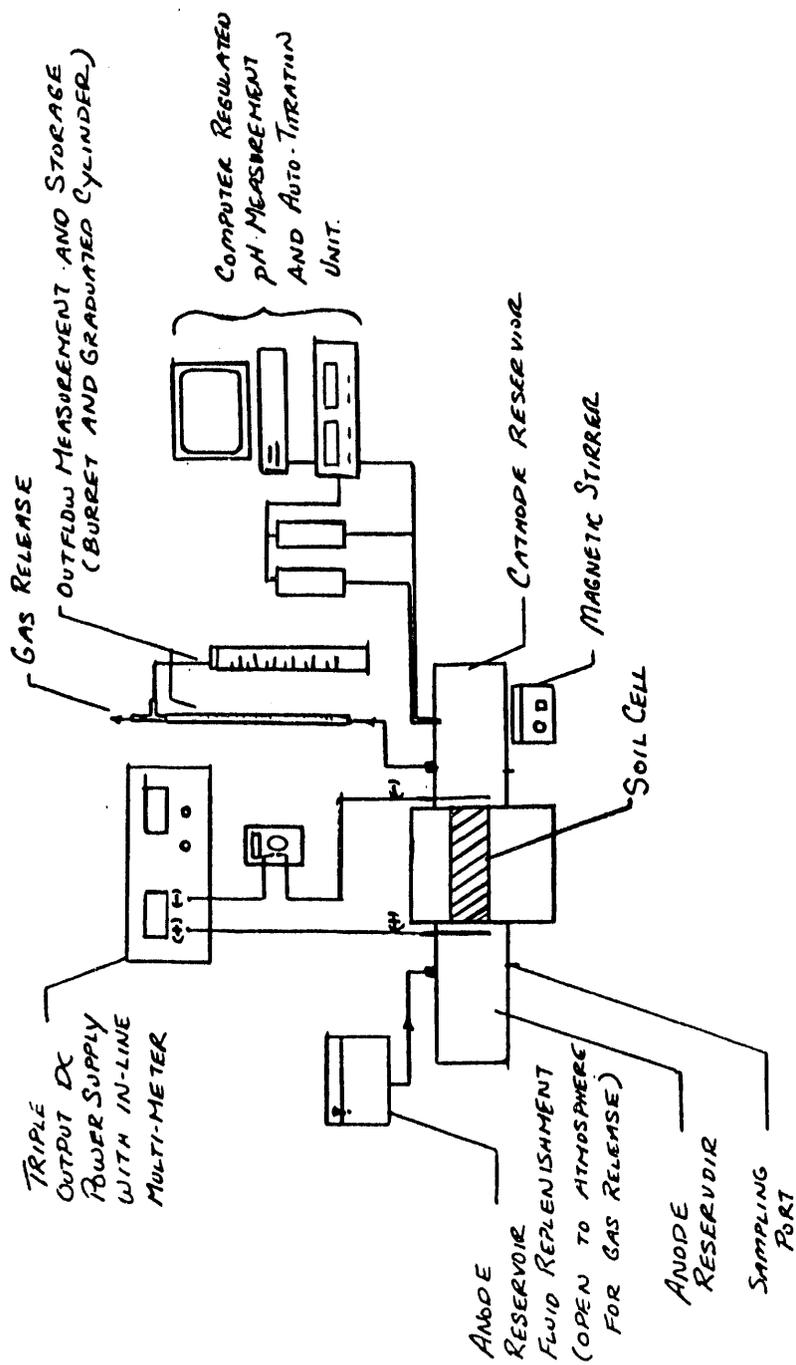


Figure 4.1. Schematic of the EK Soil Flushing Experimental Setup.

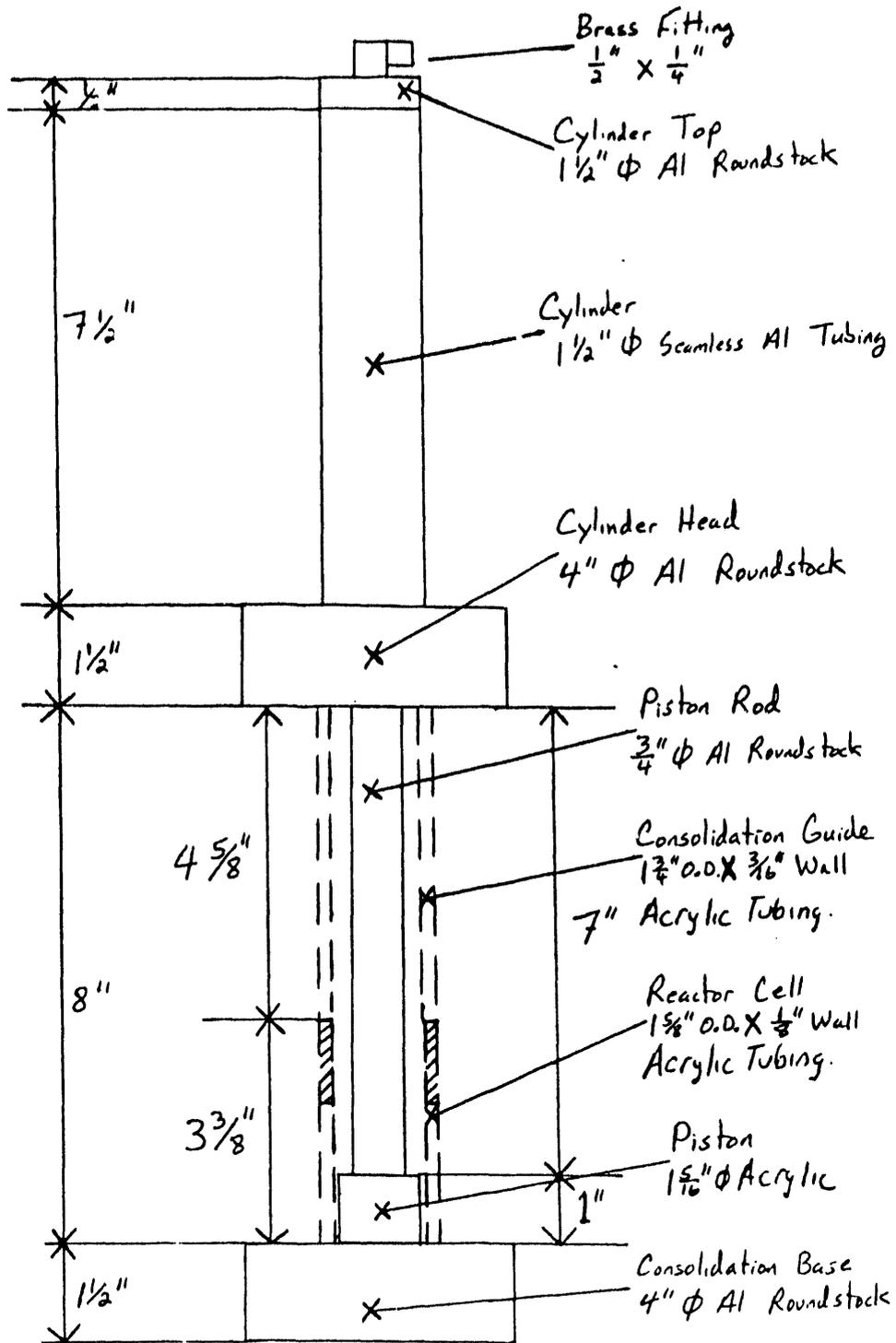
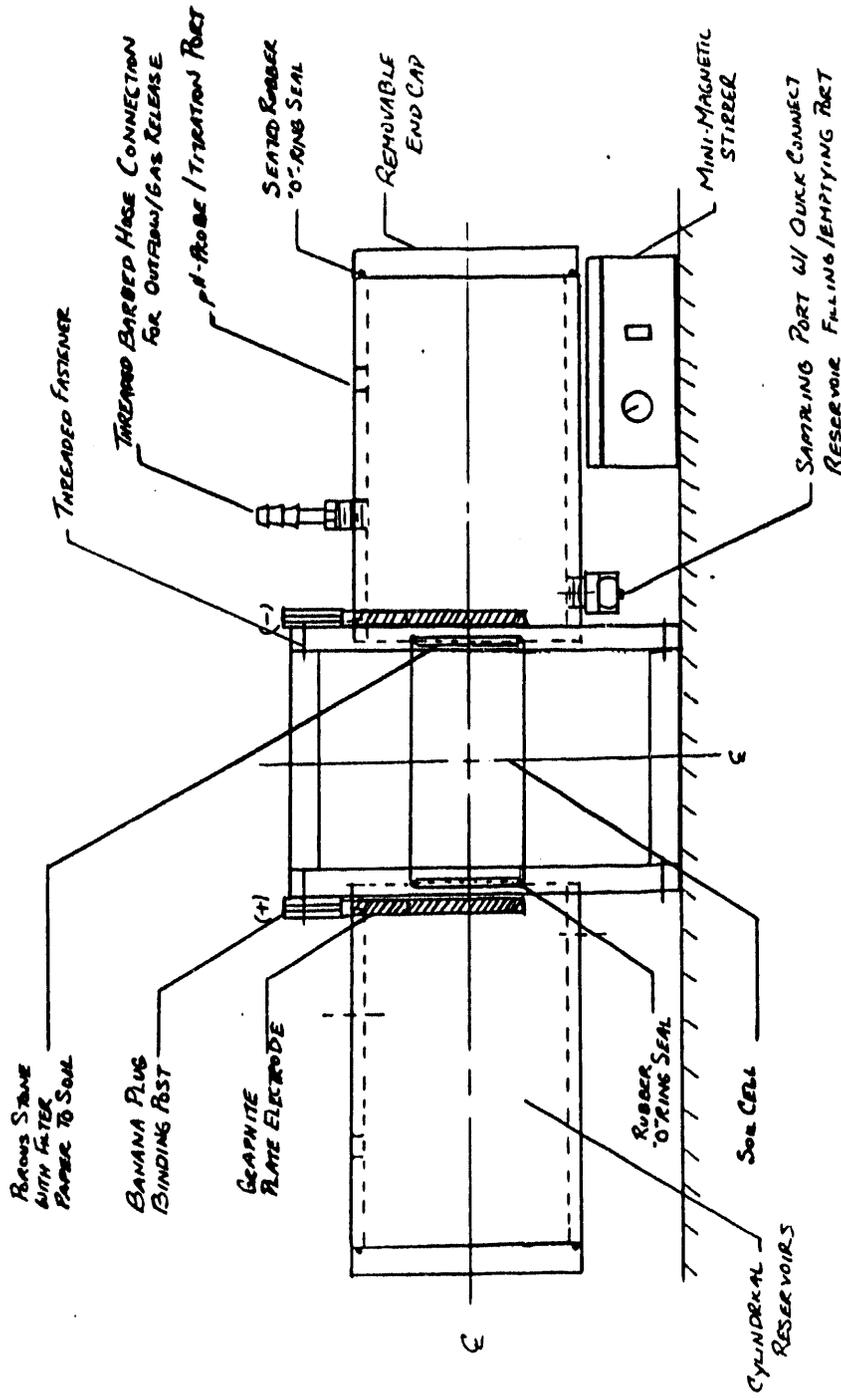


Figure 4.2. Schematic of the Soil Consolidation Unit.



SCALE: DRAWN TO 1/2 SCALE

NOTE: BOTH SIDES SYMMETRIC FROM VERTICAL CENTER LINE

Figure 4.3. Schematic of the EK Soil Flushing Reactor.

consolidators and six EK reactors were constructed. Materials used to construct the units are indicated on the drawings.

#### 4.3.2 Apparatus Testing

**Consolidation Apparatus:** Soils must be consolidated prior to placement in the EK reactor. To ensure experimental reproducibility, a consistent and reliable method of consolidation must be identified. Uncontaminated soil was used in consolidation experiments. Approximately 48 hours was required to complete the consolidation of one soil sample. The consolidation procedure developed by Pamukcu *et al.* (1991) was used and is described in the following paragraphs.

1. Soil was crushed and passed through a number 10 sieve to remove gravel or large organic material.
2. Tap water was added to approximately 200 g of soil to form a slurry having a water content of about 60 percent. The actual water content of the slurry was measured and recorded prior to consolidation. For several experiments, electrolyte ( $\text{NaNO}_3$ ) was added to the tap water to change the conductivity of the pore water.
3. The soil slurry was mixed for 5 minutes with a soil mixer to break up any clumps, reduce the amount air voids, and provide a homogeneous mixture.
4. The soil slurry was poured into the reactor cell and consolidation guide, leaving about 2 inches of clear space near the top of the guide. The pneumatic piston is then placed in the consolidation sleeve and secured.
5. Pressure regulators were used to adjust the air pressure to the consolidation devices which applies the consolidation pressure to the soil specimen. The consolidation devices were calibrated to determine the amount of air gauge pressure needed to produce the desired consolidation pressures at the piston and soil interface. The amount of consolidation was measured as the amount of piston movement. The soil sample was consolidated using the pressure schedule listed in Table 4.2.

**Table 4.2. Pressure Schedule Used  
For Soil Consolidation**

Pressure (psi)	Duration (hr)
5.0	2.0
10.0	2.0
15.0	10.0
20.0	10.0
25.0	2.0
30.0	2.0

6. After consolidation, the reactor cell containing the consolidated soil was removed from the consolidator and trimmed so that porous stones and filter paper could be placed at each end. The reactor cell, intact with consolidated soil specimen, filter paper, and porous stones was then placed into the EK reactor. The water content of the consolidated soil was determined using the trimmed soil.

**Electrokinetic (EK) Reactor:** The EK reactor utilizes a Triple Output DC Power Supply. Each power supply has the capability of powering two separate electrokinetic reactors with constant current or voltage. The power supply is capable of providing 30 volts of electricity to two separate reactors, or it may also be hooked up in series operation to obtain a maximum output of 60 volts to a single reactor.

The test soil is contained in the same acrylic cylinder used for the consolidation. The reactor cell is placed between the two reservoirs. A pair of inert graphite plate electrodes are used to apply the electric current to the soil cell. The electrodes are directly submerged in water contained by reservoirs adjacent to each end of the soil cell. Flow measurement is accomplished by graduated burettes connected to the top of each reservoir. The burettes are opened to the atmosphere to allow for the passage and release of gas generated from electrolysis reactions. Sampling ports are located at the bottom of each reservoir to allow for removal of reservoir water for analysis. Each reservoir was designed to allow for the insertion of a pH probe and reservoir conditioning. The reservoirs are also elevated to allow for a mini- magnetic stirrer to be placed below them, to be used in conjunction with conditioning. A multimeter was used to attain accurate measurements of the magnitude of the current, voltage drop, and resistance between the electrodes.

The initial testing of the EK reactor consisted of determining the water movement with respect to time (measured as the amount of water discharged at the cathode) as a function of ionic strength of the soil slurry make-up and reservoir water. Constant voltage (30 volts) conditions were employed. The pH and the conductivity of the electrode reservoir water were also monitored.

#### **4.4 REMEDIATION OF LEAD-CONTAMINATED SOIL USING EK FLUSHING**

The ability of electrokinetics to remediate a lead contaminated soil was tested under a variety of conditions. Table 4.3 contains a summary of the experimental conditions used in this phase of the study. Tests 1 through 10 involved reactor testing and method development thus, the results from these tests are not presented. A description of the methodology used for the remediation experiments is presented in subsequent paragraphs.

**Table 4.3. Summary of Experimental Conditions Used for EK-Soil Remediation**

Test No.	No. of Replicate	Initial Soil Pb, mg/kg	Applied Voltage, V	Anode Reservoir	Cathode Reservoir	Test Conditions <sup>1</sup>
11	3	1000	30	500 $\mu\text{mho}^2$	500 $\mu\text{mho}$	1000/30/500/500
12	3	1000	30	DI Water	DI Water	1000/30/DI/DI
13	2	150	30	565 $\mu\text{mho}$	565 $\mu\text{mho}$	150/30/500/500
14	2	1000	30	DI Water	1 M HAc <sup>3</sup>	1000/30/DI/HAc
15	3	1000	60	500 $\mu\text{mho}$	500 $\mu\text{mho}$	1000/60/500/500
16	3	150	60	DI Water	1 M HAc	150/60/DI/HAc
17	3	1000	60	500 $\mu\text{mho}$	1 M HAc	1000/60/500/HAc
18	3	150	60	500 $\mu\text{mho}$	1 M HAc	150/60/500/HAc
19	3	150	60	500 $\mu\text{mho}$	500 $\mu\text{mho}$	150/60/500/500
20	3	1000	60	0.1 N HCl	1 M HAc	1000/60/HCl/HAc

<sup>1</sup> Pb concentration/Voltage./Anode Condition/Cathode Condition: To Be Used as Test Condition Identifier in Subsequent Tables and Discussion.

<sup>2</sup> Conductivity was altered using  $\text{NaNO}_3$ .

<sup>3</sup> Acetic Acid.

After consolidation, the soil sample contained in an acrylic sleeve was placed horizontally into an EK reactor apparatus. Porous stones and 8 micron filter paper were attached to each end of the soil sample. The reservoirs surrounding the electrodes were filled with the desired conditioning fluid and a constant voltage (either 30 or 60 V) was applied. An open flow arrangement was utilized for measuring the volume of effluent flow and for venting of gases produced during electrolysis. Effluent flow was collected in a graduated cylinder and stored in sample bottles for later analyses. A constant, negligible hydraulic gradient was maintained across the soil specimen by use of a Mariotte bottle connected to the anode side of the reactor. During EK processing, the pH, conductivity, and Pb content of the anode and cathode reservoirs were monitored. The current and liquid flow resulting from the applied voltage were also measured with time. EK flushing experiments continued until a specific number of pore volumes of flow were passed through the soil sample or flow cessation occurred.

After EK flushing, the soil specimen was extracted from the cell and sliced into eight equal length sections. Each section was analyzed for moisture content, pH, conductivity, and Pb concentration. The pH and conductivity were determined by mixing 5 gm of soil from each slice with 25 mL of deionized water and analyzing with a standard pH and conductivity meter. A 1:1 ratio of soil to water for these analysis could not be performed due to the small quantity of soil in each section. However, the 1:5 ratio does provide for a relative determination of the pH and conductivity distribution through the soil sample. Pb concentrations were determined by an acid digestion procedure that consisted of mixing 5 gm of soil from each slice with 40 mL of 5.0 N nitric acid (1:8) and shaking for 48 hours. After digestion, the mixture was vacuum filtered through a 0.45 micron filter and analyzed for Pb by flame atomic absorption (A.A.) spectrophotometry according

to USEPA Method 7420. Lead content of the trimmed soil samples (from each end) were determined in an identical manner. The initial lead concentration of the soil specimen were assumed to be equal to the trimmed soil Pb content. In Figure 4.4, the soil Pb content versus normalized distance from the anode is presented for a soil specimen that did not undergo EK flushing. The concentration of lead is consistent throughout the soil sample thus, in EK flushing experiments it can be assumed that the lead distribution in the soil is homogenous.

#### 4.5 QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) is an important factor in the success of a research project. The purpose of implementing QA procedures is to insure that the methods used in collecting and processing data are valid and reliable. Elements of a QA plan include using accepted analytical methods, following standard operating procedures, and instituting quality control (QC) testing procedures.

Samples and analyses conducted during the course of this proposed study were conducted at the Environmental Engineering laboratories at West Virginia University. Analyses conducted included Pb concentrations in the soil and aqueous phase, pH, conductivity, voltage drop, and current. In addition to these analyses, various soil characterization tests (see Table 4.1) were conducted. For these tests, well-established protocols were followed such as *Standard Methods for the Examination of Water and Wastewater*, *Testing Methods for Evaluating Solid Waste: Physical/Chemical Methods*, and the *Annual Book of ASTM Standards*. Recoveries of Pb for the atomic absorption (A.A.) spectrophotometer measurements are presented in Table 4.4. The excellent Pb recoveries reported in Table 4.4 demonstrate the reliability of Pb measurement on the A.A. The majority of the bench-scale tests were conducted in triplicate (mean values and standard deviations for these test are presented in the Results and Discussion section). All experimental data and observations were recorded in permanent ink in laboratory notebook with carbon copies. Results were continuously monitored and processed to detect improper procedures or inconsistent results. Data were entered on a computerized data management package to facilitate data manipulation and analyses.

**Table 4.4 Lead Recoveries From A.A. Analyses**

Range = 94 - 110
Mean = 102.4
Standard Deviation = 4.0
Median = 102

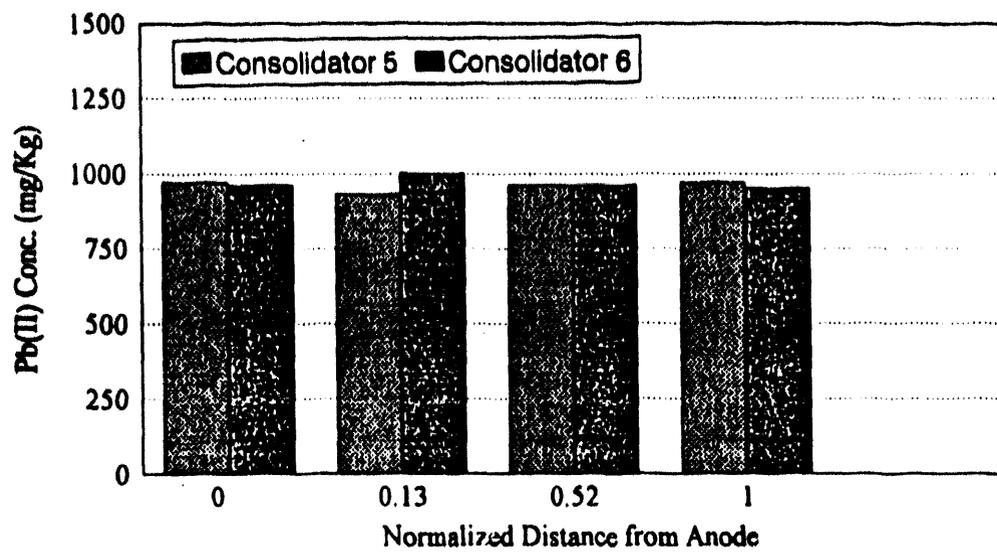


Figure 4.4. Soil Pb Concentration Versus Normalized Distance from the Anode for a Soil Speciman That Did Not Undergo EK Soil Flushing.

## 5. RESULTS AND DISCUSSION

In this section, results from soil selection and characterization, soil contamination and decontamination batch experiments, and the remediation of lead-contaminated soil via electrokinetics are presented and discussed. For the reader's convenience, the results from each class of experiments are presented and discussed separately.

### 5.1 SOIL SELECTION AND CHARACTERIZATION

The study soil was classified as a "Collamer silt loam" by the Soil Conservation Service. Values for the study soil's chemical and physical parameters are presented in Table 5.1. The "±" value represents one standard deviation from the average.

**Table 5.1. Chemical and Physical Parameters of Study Soil**

Parameter	Value
Soil pH (1:1 soil:water)	5.6 ± 0.03
Soil pH (1:5 soil:water)	6.5 - 7
Indigenous Lead Content, mg/kg	22.8 ± 0.3
CEC, meq/100 g soil	25.6 ± 0.60
Total Volatile Solids, %	5.53 ± 0.20
Total Metal Content, mg/kg	
Fe	12,800 ± 20
Al	10,350 ± 20
Mn	118 ± 2
Free Iron Oxide, mg/kg	3700 ± 120
Amorphous Iron Oxide, mg/kg	2600 ± 70
Amorphous Aluminum Oxide, mg/kg	850 ± 90
Amorphous Manganese Oxide, mg/kg	18 ± 5
Hydraulic Conductivity, cm/sec	5.1 x 10 <sup>-8</sup>
Particle Size Distribution, % passing sieve <sup>1</sup>	
No. 10 (2 mm)	96.5
No. 20 (0.85 mm)	75.8
No. 40 (.425 mm)	57.5
No. 60 (0.25 mm)	47.1
No. 100 (.149 mm)	40.6
No. 200 (.0075 mm)	30.5

<sup>1</sup> Average of two tests.

The pH of the study soil was about 5.6 when a soil:water ratio of 1:1 was used and was between 6.5 and 7 when a soil:water ratio of 1:5 was employed. A higher pH was observed for the 1:5 soil:water ratio because of dilution. The 1:5 soil:water pH method was used throughout this study

because in the EK soil flushing experiments there was not enough soil to measure the pH using a 1:1 soil:water ratio. Using the 1:5 method will not significantly affect the results as the relative changes in pH between tests and soil segments will be compared. The indigenous lead content of the soil was about 23 mg/kg, which is in the normal background range for lead. The soil had a cation exchange capacity (CEC) of approximately 27 milliequivalents/100 g soil, making it an "active" soil. The organic matter content of the soil was approximately 5.5 percent. A fair number of the exchange sites are most likely associated with the organic portion of the soil. The remainder of the exchange sites are associated with various metal oxides and surface imperfections. The total metal content of the soil is the summation of the metal present as constituents of sand particles, layer silicates, organic matter, and metal oxides. Free iron oxide content (measured by the Dithionite extraction procedure) roughly approximates the amount of iron associated with crystalline and amorphous iron oxides. For the study soil, about 29 percent of the total iron was present as free iron oxides. The amorphous iron oxide content (measured by the AAO extraction procedure) was about 2600 mg/kg. Amorphous iron oxides are highly effective metal scavengers. The aluminum content of the soil was 10,350 mg/kg. The total aluminum content is generally large for soils with significant amounts of layered silicates, since Al is the primary constituent in the octahedral layers of 1:1 and 2:1 clays (see Figure 3.3). Approximately 8 percent of the total aluminum was present as amorphous oxides (source of metal retention). As expected, the total manganese content of the soil was much smaller than the total iron and aluminum contents. The total Mn content of soils generally consist of manganese oxides and manganese found in layered silicates as a result of isomorphous substitution. The Mn oxide content was about 18 mg/kg and, as with Fe and Al amorphous oxides, represents a sink for metal retention.

The soil had a very low hydraulic conductivity, less than  $10^{-7}$  cm/s. If this soil was from a contaminated site, *in-situ* technologies that use hydraulic pumping would not be feasible because of the difficulty in promoting water movement. The soil's particle size distribution is presented in Table 5.1 and is presented in terms of ASTM 422 particle size classification in Table 5.2. The study soil is a heterogeneous mixture made up of about two-thirds medium and fine sands and one-third silts and clays.

**Table 5.2 ASTM 422 Particle Size Classification**

% Coarse Sand <sup>1</sup>	3.5
% Medium Sand <sup>2</sup>	39.1
% Fine Sand <sup>3</sup>	27.0
% Silt and Clay <sup>4</sup>	30.5

<sup>1</sup> Passing No. 4 Sieve and Retained by No. 10 Sieve.

<sup>2</sup> Passing No. 10 Sieve and Retained by No. 40 Sieve.

<sup>3</sup> Passing No. 40 Sieve and Retained by No. 200 Sieve.

<sup>4</sup> Passing No. 200.

The net acid-base titration curve for the study soil is presented in Figure 5.1. As mentioned previously in Chapter 4, the net titration curve was developed by subtracting the titration curve of the ionic solution from the titration curve of a 20 g/L soil suspension. Approximately 0.0125,

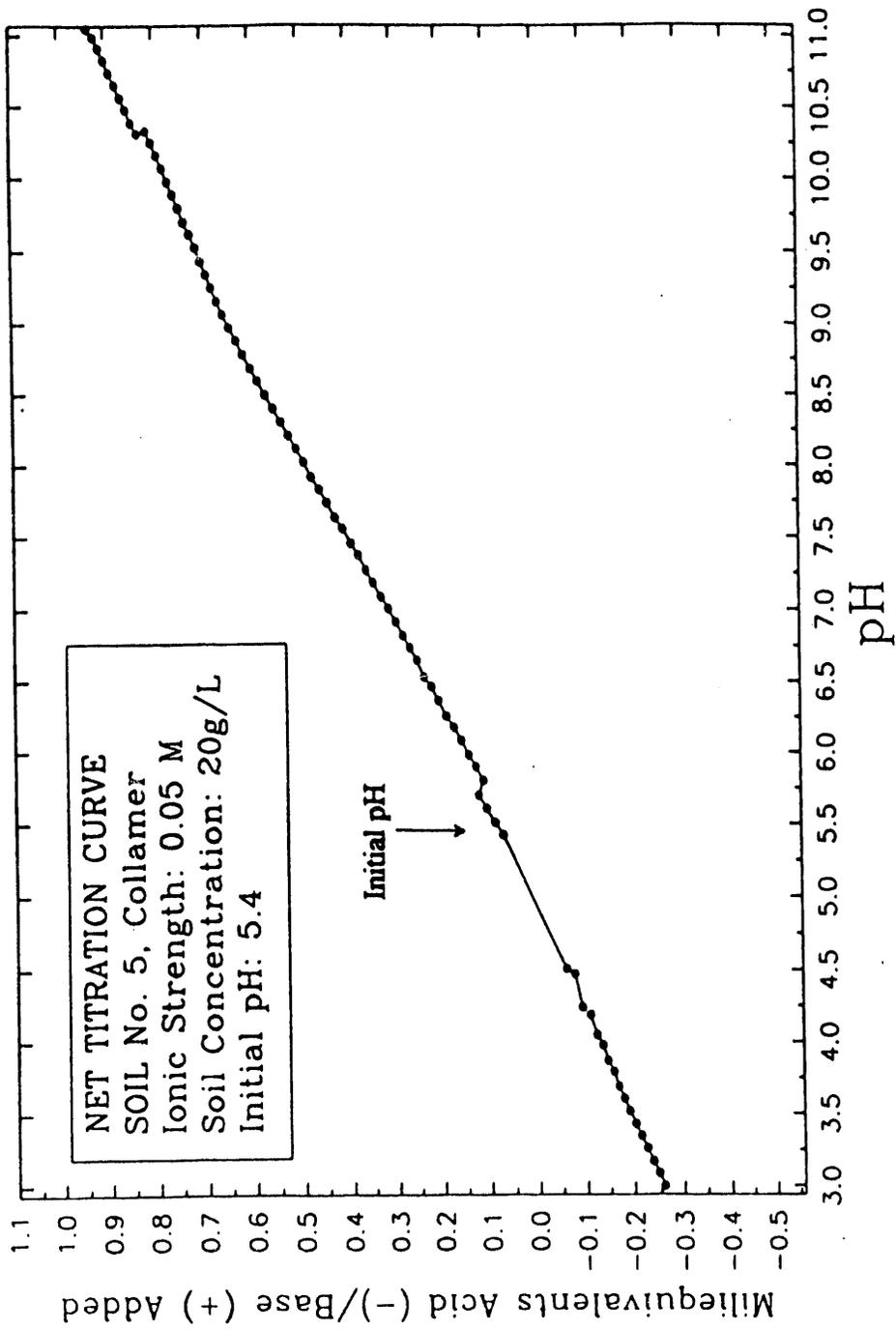


Figure 5.1. Net Titration Curve for the Study Soil

0.0075, and 0.0025 milliequivalents (meq) of strong acid per gram of soil were required to reduce the soil pH to 3, 4, and 4.5, respectively. At lower pHs more acid is required to alter the pH because of complexation and dissolution of metal oxides. This is important because metal desorption is a strong function of pH. As will be discussed later, lead removal during EK soil flushing began when the soil pH was near 4 and was essentially complete when the pH was near 3.

In summary, the study soil has a fairly high CEC, organic matter content, metal oxide content, and buffering capacity. The study soil is an excellent retainer of heavy metals, has a low hydraulic conductivity, and has significant amounts of sands, silts, and clays. Thus, the soil is an excellent candidate for electrokinetic flushing. Because a real soil was used (*i.e.*, not a pure clay), the results from EK soil flushing experiments present herein are more representative of what can be expected at contaminated sites. The use of an actual soil to test the efficacy of EK soil flushing was forwarded at the DOE sponsored workshop on electrokinetics (DOE, 1992) as a research topic requiring attention.

## 5.2. SOIL CONTAMINATION AND DECONTAMINATION BATCH EXPERIMENTS

As described earlier, the study soil was contaminated with 10, 100, and 1,000 mg/L Pb solutions using a 10:1 liquid:soil ratio. The contaminated soil then underwent batch soil decontamination tests to ascertain the behavior of soil-bound lead during EK flushing. The results from these two sets of experiments are presented in the next two sections.

### 5.2.1 Batch Soil Contamination

Soil lead concentrations obtained from the three artificial contaminations are presented graphically in Figure 5.2. Approximately 96, 99, and 83 percent of the aqueous lead was sequestered by the soil for initial lead concentrations of 10, 100, and 1,000 mg/L, respectively. Two methods of determining soil lead concentrations were used: A mass balance approach and USEPA Method 3050 (a strong acid-hydrogen peroxide digestion). The following equation represents the approach used for the mass balance calculations:

$$\text{Soil Pb} = \{[\text{Pb}_o \cdot V_o] - [\text{Pb}_f V_f]\} + [W_s]$$

where

$\text{Pb}_o$  = Initial Pb Concentration.

$\text{Pb}_f$  = Final Pb Concentration.

$V_o$  = Initial Volume Pb Solution.

$V_f$  = Supernatant Volume.

$W_s$  = Weight Soil Added.

The results from the two methods are presented in Table 5.3. The difference between the mass balance approach and the USEPA Method 3050 was less than 10 percent. The values in parenthesis represents the average of triplicate tests. Given the closeness of the results from the two methods, the average of the mass balance and Method 3050 results was used to determine batch soil decontamination efficiencies.

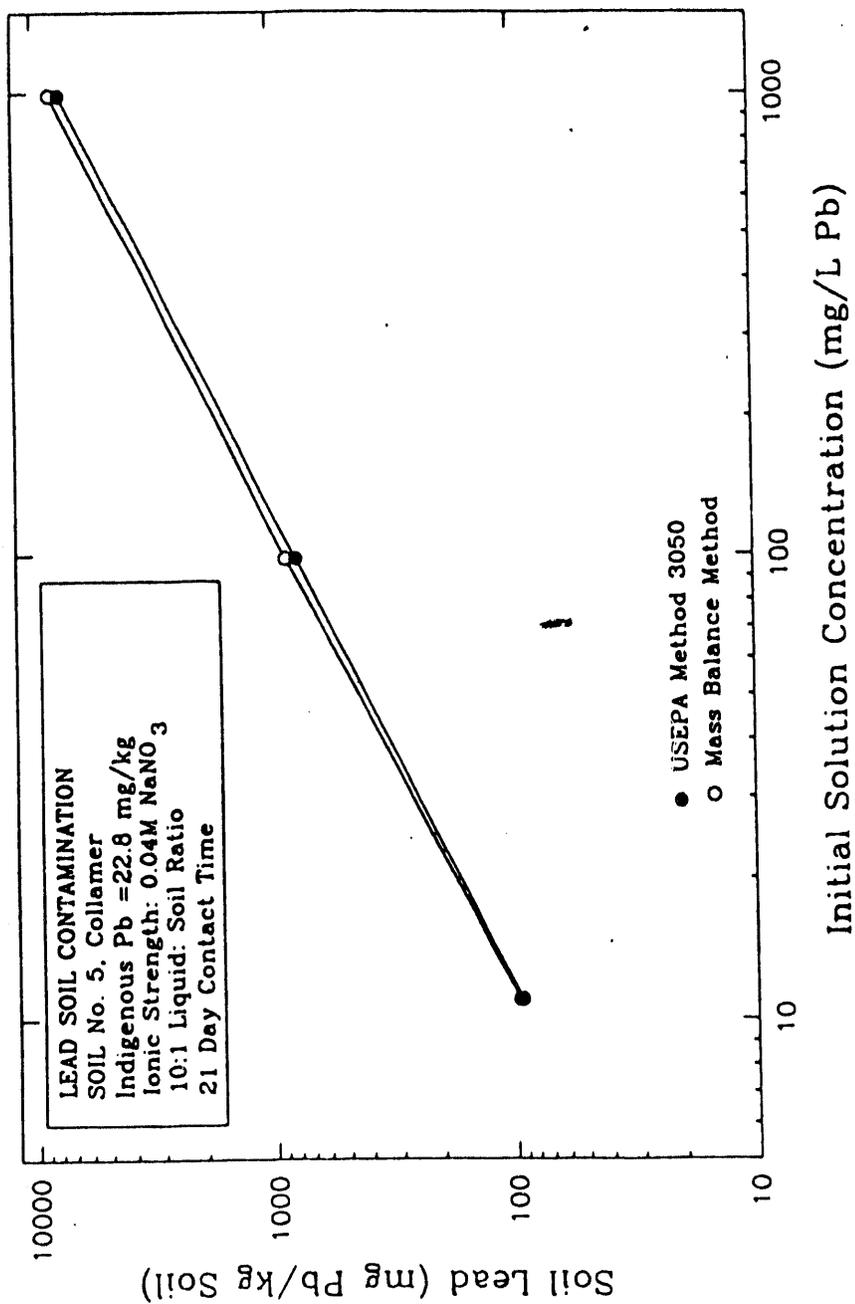


Figure 5.2. Lead Contamination Results for the Study Soil

**Table 5.3. Lead Concentrations From Mass Balance and USEPA Method 3050**

10 mg/L Pb		100 mg/L Pb		1,000 mg/L Pb	
EPA 3050	MB <sup>1</sup>	EPA 3050	MB <sup>1</sup>	EPA 3050	MB <sup>1</sup>
94.0-94.7 (93.5)	97.0	793-802 (799)	878	7500-7790 (7620)	8360

<sup>1</sup> Mass Balance

### 5.2.2 Batch Decontamination Experiments

In order to assess the behavior of soil-bound lead under electrokinetic conditions, the contaminated soil was extracted with the washing solutions listed in section 4.2.2. Acids were employed to simulate the conditions that occur as the pH-front moves from the anode to the cathode.  $\text{CaCl}_2$  was used to replicate the behavior of soil-bound lead as the conductivity of the pore water solution is increased. EDTA, a strong complexing agent, was used to assess its possible use as a desorptive additive to the EK process. Tap water was used to provide a benchmark.

In Figure 5.3, results from batch washing tests are presented for the three lead contamination levels employed. For all contamination levels, tap water was an ineffective extractant strongly indicating that the lead is bound on the soil surface and not the pore or bound water. As expected, both nitric and hydrochloric acids were very effective in removing lead from the soil. The acids lowered the pH of the soil suspension to about 2, which strongly favored desorption. Acetic acid was less effective than the strong acids in desorbing lead. The pH of the acetic acid experiments were about 4.5, compared to about 2 for the strong acids. Based on these results, it can be concluded that the pH of the soil during EK soil flushing will have to decrease well below 4.5 if large amounts of lead are to be removed. There was a slight concentration effect for the acids - the higher concentration of acid was slightly more effective. EDTA, a strong metal complexation agent, was also very effective in removing lead from the soil and there did not appear to be a concentration effect.  $\text{CaCl}_2$  was moderately affective in desorbing lead and there was a noticeable concentration effect. The predominant lead removal mechanism in the presence of  $\text{CaCl}_2$  is most likely ion exchange with  $\text{Ca}^{2+}$ . Since a large amount of the lead was not removed through exchange by  $\text{Ca}^{2+}$ , one may assume that lead is bound by mechanisms other than ion exchange (*e.g.*, surface complexation by organic matter and metal oxides).

The results from the batch decontamination experiments indicate the lead will be removed from the soil during EK flushing if the low pH front moves completely through the soil. The increase in ionic strength (conductivity) during EK flushing will also improve lead desorption. If EDTA is added to the reservoir water(s), lead desorption from the soil to the pore liquid may increase but lead movement into the reservoir waters may decrease. EDTA-Pb complexes are negative thus, transport by ion migration (towards the anode) will oppose transport by advection (towards the cathode).

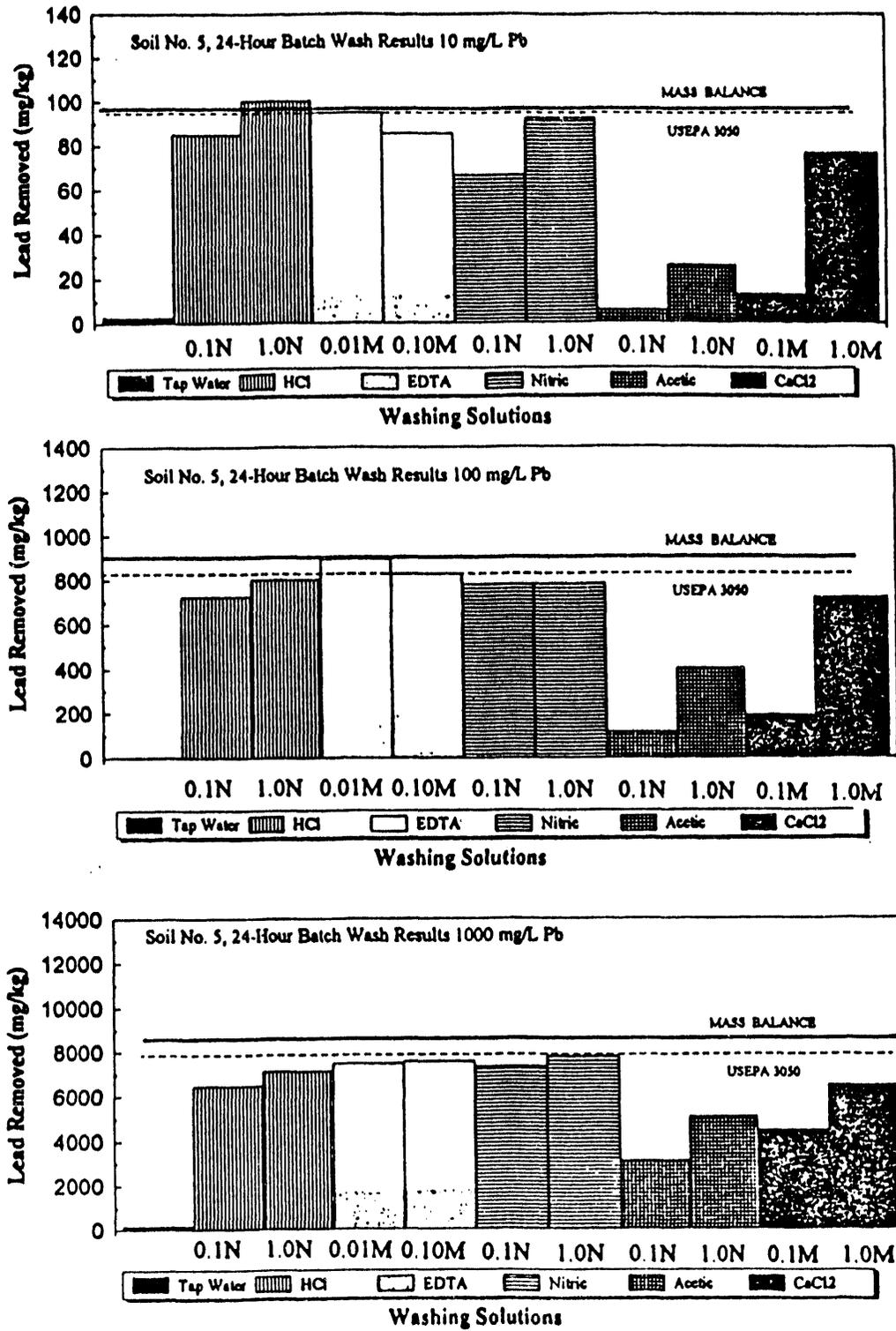


Figure 5.3. Results From Batch Washing Experiments

### 5.3 REMEDIATION OF LEAD-CONTAMINATED SOIL USING EK FLUSHING

In this section results from electrokinetic soil flushing experiments are presented. Results from the EK experiments take on two forms: Water movement and current as a function of time, and soil lead and soil pH as a function of distance from the electrodes. For the reader's convenience Table 4.3, a summary of the experimental conditions used, is repeated below.

**Table 4.3. Summary of Experimental Conditions Used for EK-Soil Remediation**

Test No.	No. of Replicate	Initial Soil Pb, mg/kg	Applied Voltage, V	Anode Reservoir	Cathode Reservoir	Test Conditions <sup>1</sup>
11	3	1000	30	500 $\mu\text{mho}^2$	500 $\mu\text{mho}$	1000/30/500/500
12	3	1000	30	DI Water	DI Water	1000/30/DI/DI
13	2	150	30	565 $\mu\text{mho}$	565 $\mu\text{mho}$	150/30/500/500
14	2	1000	30	DI Water	1 M HAc <sup>3</sup>	1000/30/DI/HAc
15	3	1000	60	500 $\mu\text{mho}$	500 $\mu\text{mho}$	1000/60/500/500
16	3	150	60	DI Water	1 M HAc	150/60/DI/HAc
17	3	1000	60	500 $\mu\text{mho}$	1 M HAc	1000/60/500/HAc
18	3	150	60	500 $\mu\text{mho}$	1 M HAc	150/60/500/HAc
19	3	150	60	500 $\mu\text{mho}$	500 $\mu\text{mho}$	150/60/500/500
20	3	1000	60	0.1 N HCl	1 M HAc	1000/60/HCl/HAc

<sup>1</sup> Pb concentration/Voltage,/Anode Condition/Cathode Condition: To Be Used as Test Condition Identifier in Subsequent Tables and Discussion.

<sup>2</sup> Conductivity was altered using  $\text{NaNO}_3$ .

<sup>3</sup> Acetic Acid.

#### 5.3.1 Water Movement and Current

The volume of water moved and the resulting current as a function of time under a constant voltage are presented in Figures 5.4 through 5.13 for Tests 11 through 20, respectively. The volume of water transported is expressed in pore volumes (PV). On the average, the pore volume of a soil specimen was approximately  $35 \text{ cm}^3$  (mL). Current resulting from the applied voltage is expressed in milliamps. For almost all tests, the current dropped from an initially high value after about a half day of applied voltage. It is hypothesized that the initial rapid drop in current was caused by the formation and stabilizing of the electric double layer. It should be noted that the half day period represented a fraction of the total time the soil specimen was subjected to EK flushing. While the results of repeated experiments were not always in complete agreement, similar trends were observed. Given the heterogeneous nature of the soil, some variability between samples was expected (In fact, one recommendation of the DOE sponsored electrokinetic workshop (DOE 1992) was to assess the reproducibility of EK soil flushing). After the initial rapid drop, the current either remained fairly constant or declined slowly over the test duration. EK experiments

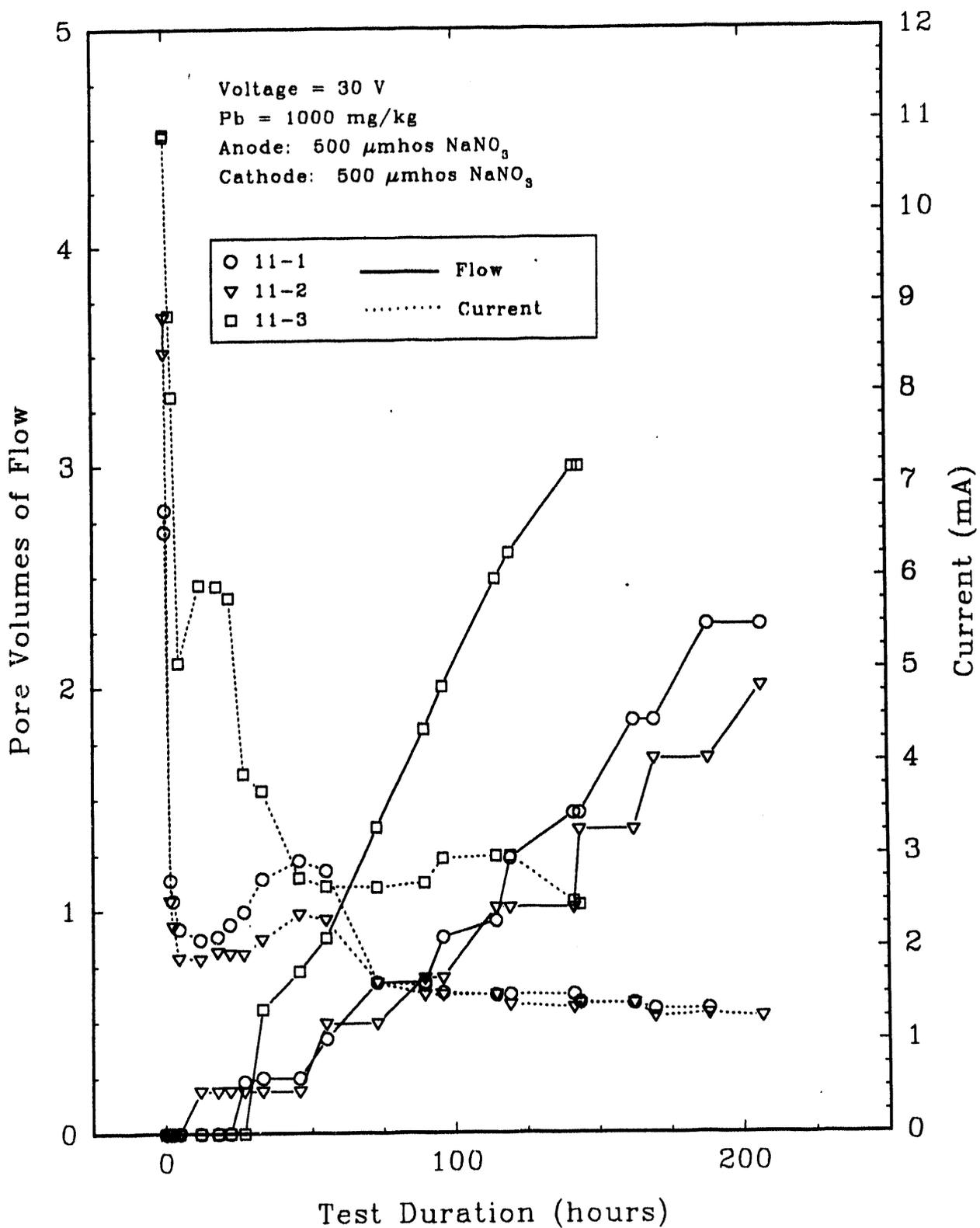


Figure 5.4. Volume of Water and Current as a Function of Time For Test 11

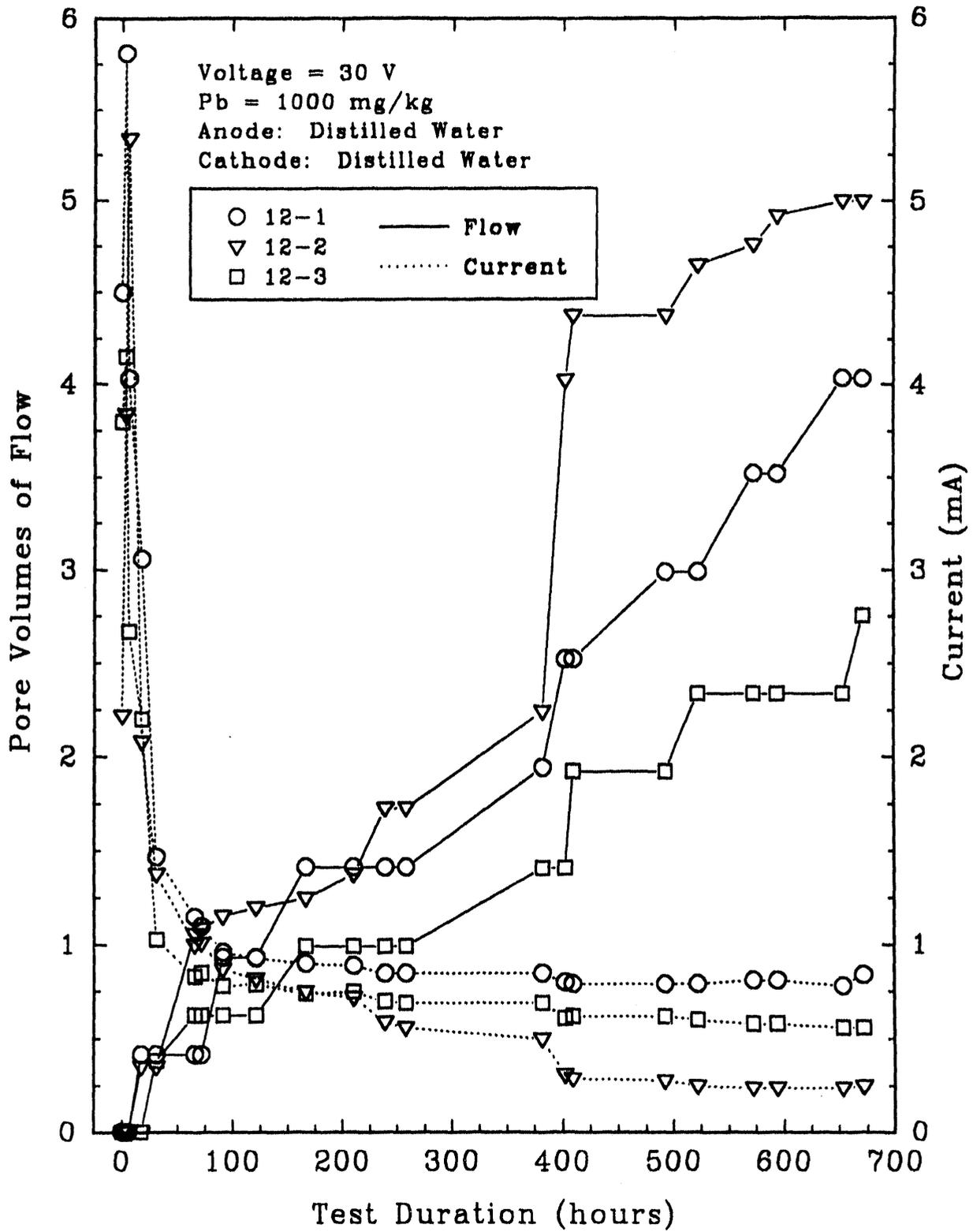


Figure 5.5. Volume of Water and Current as a Function of Time For Test 12

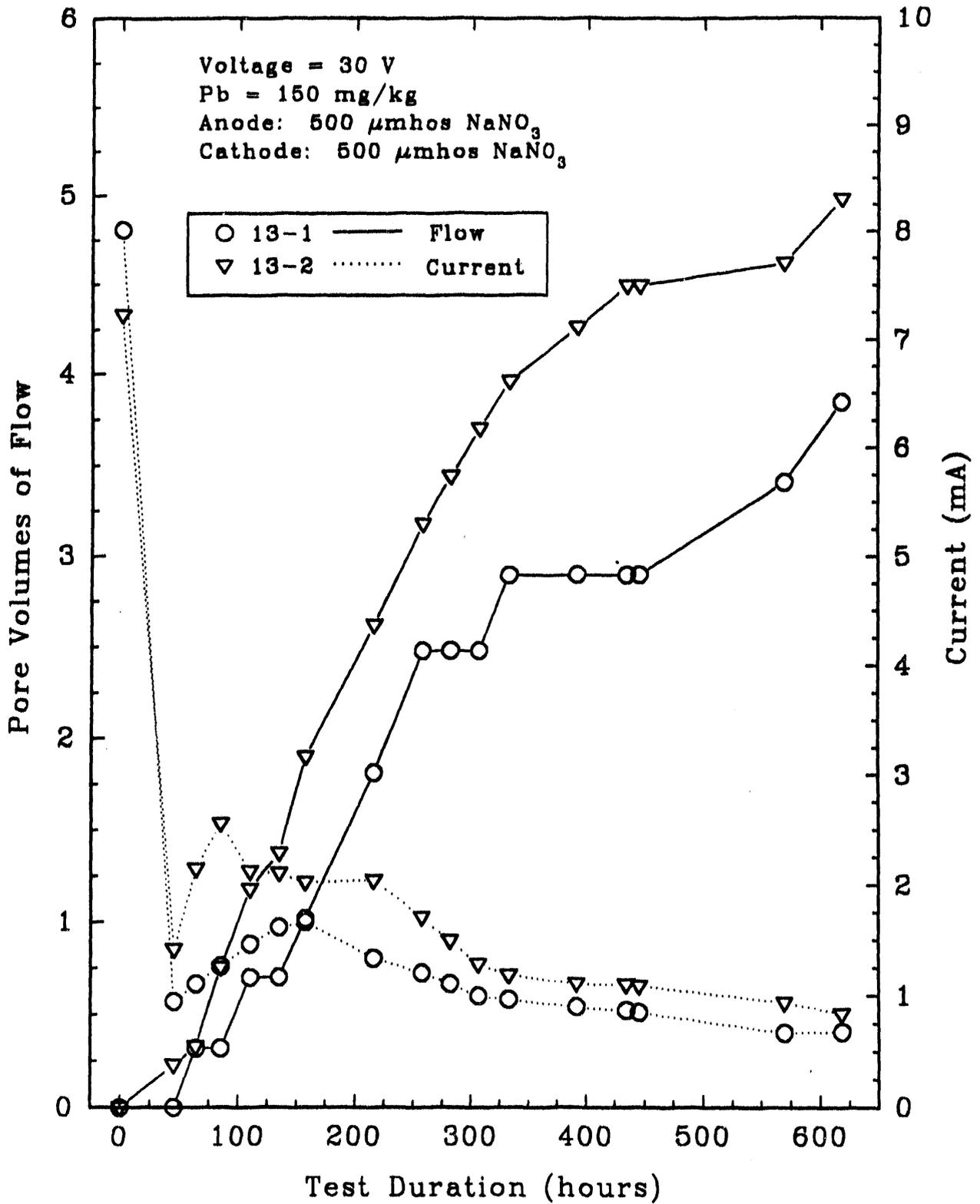


Figure 5.6. Volume of Water and Current as a Function of Time For Test 13

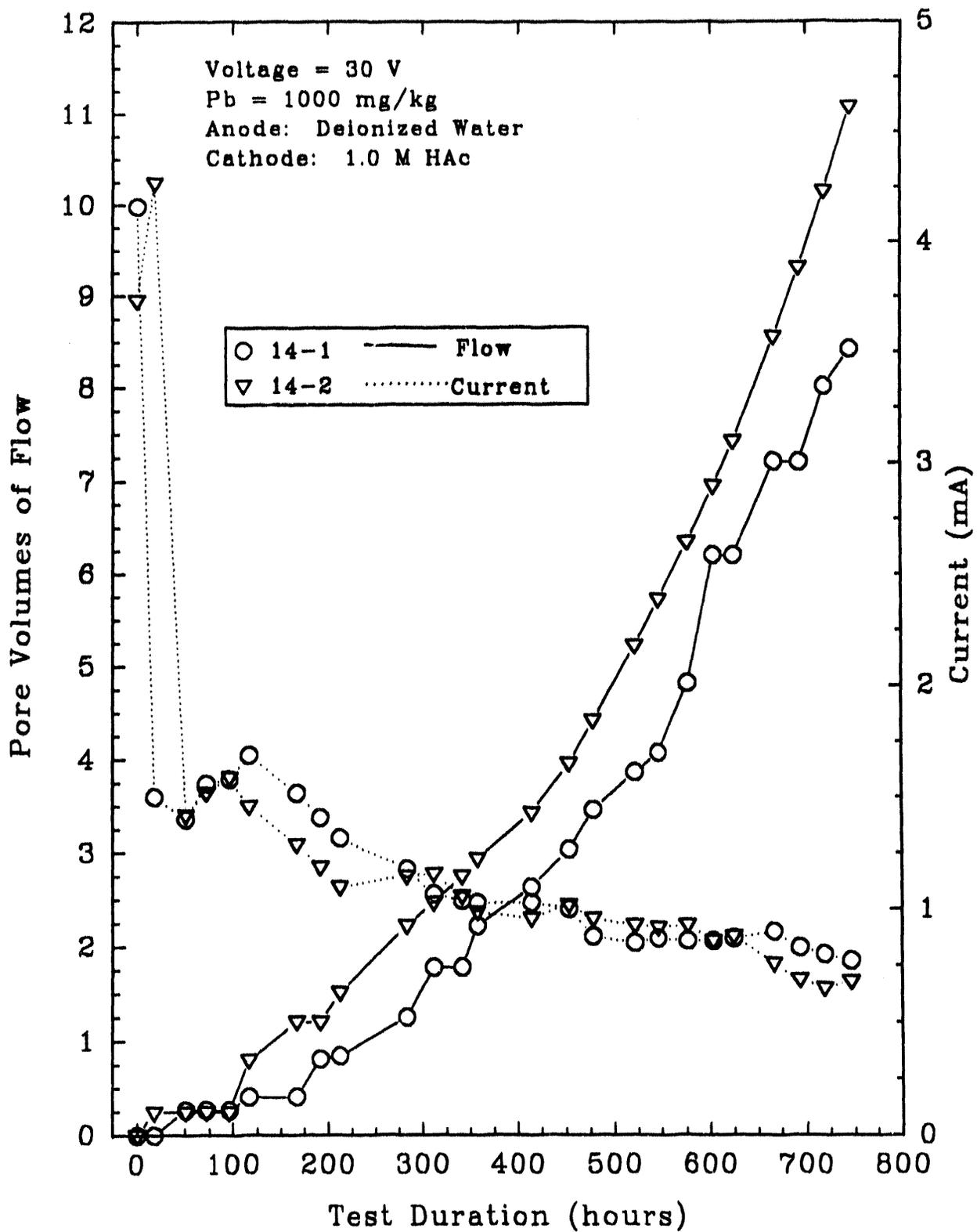


Figure 5.7. Volume of Water and Current as a Function of Time For Test 14

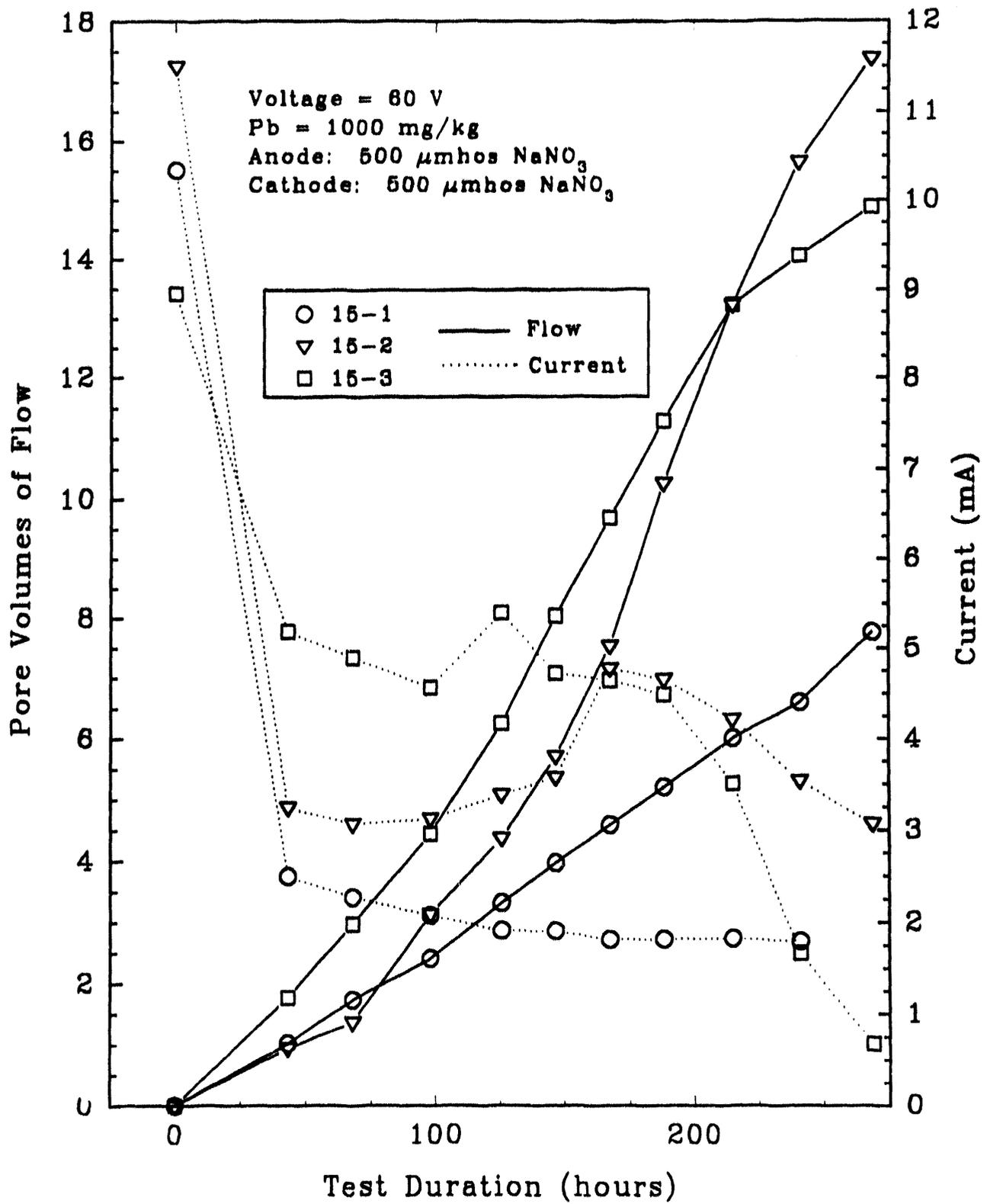


Figure 5.8. Volume of Water and Current as a Function of Time For Test 15

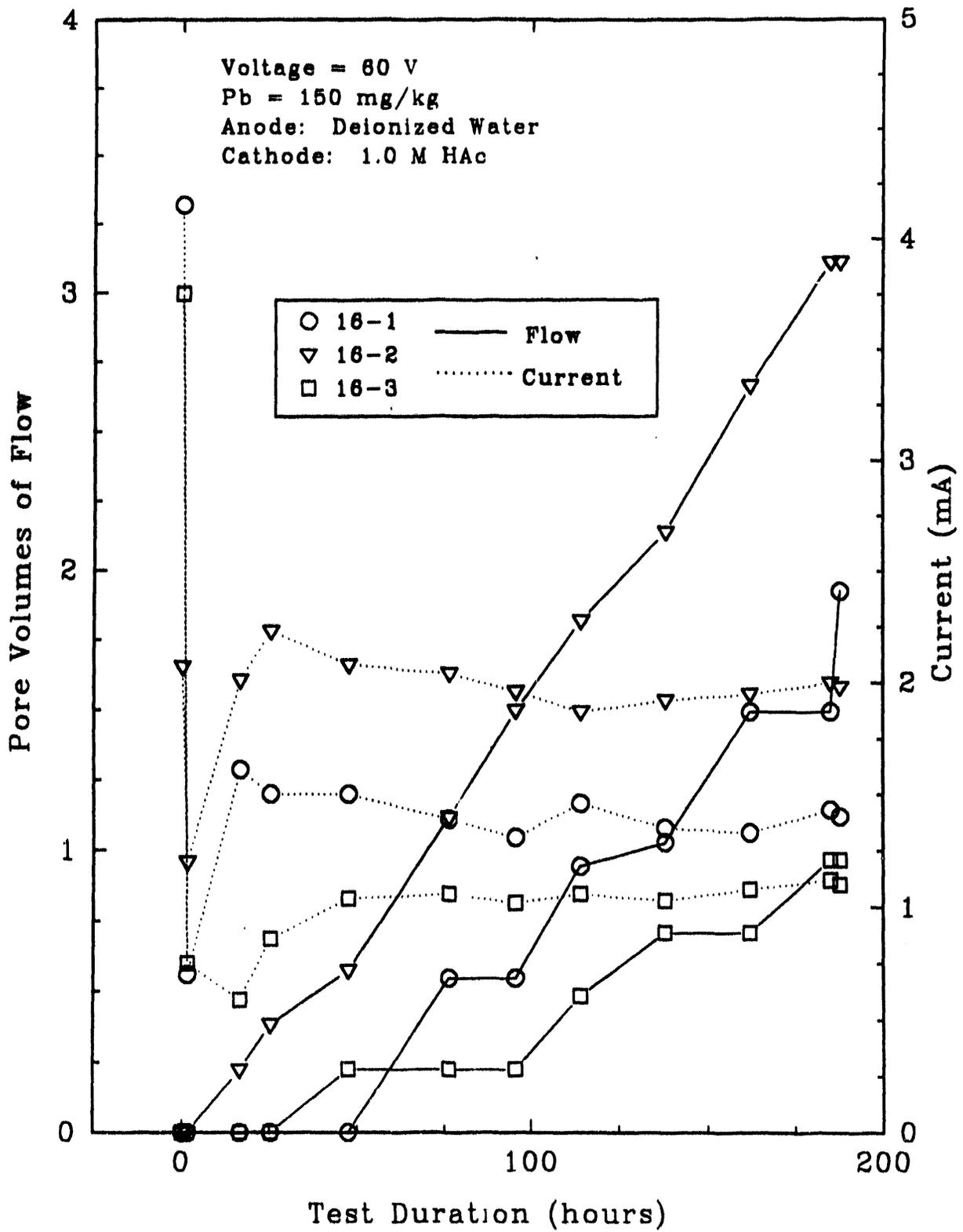


Figure 5.9. Volume of Water and Current as a Function of Time For Test 16

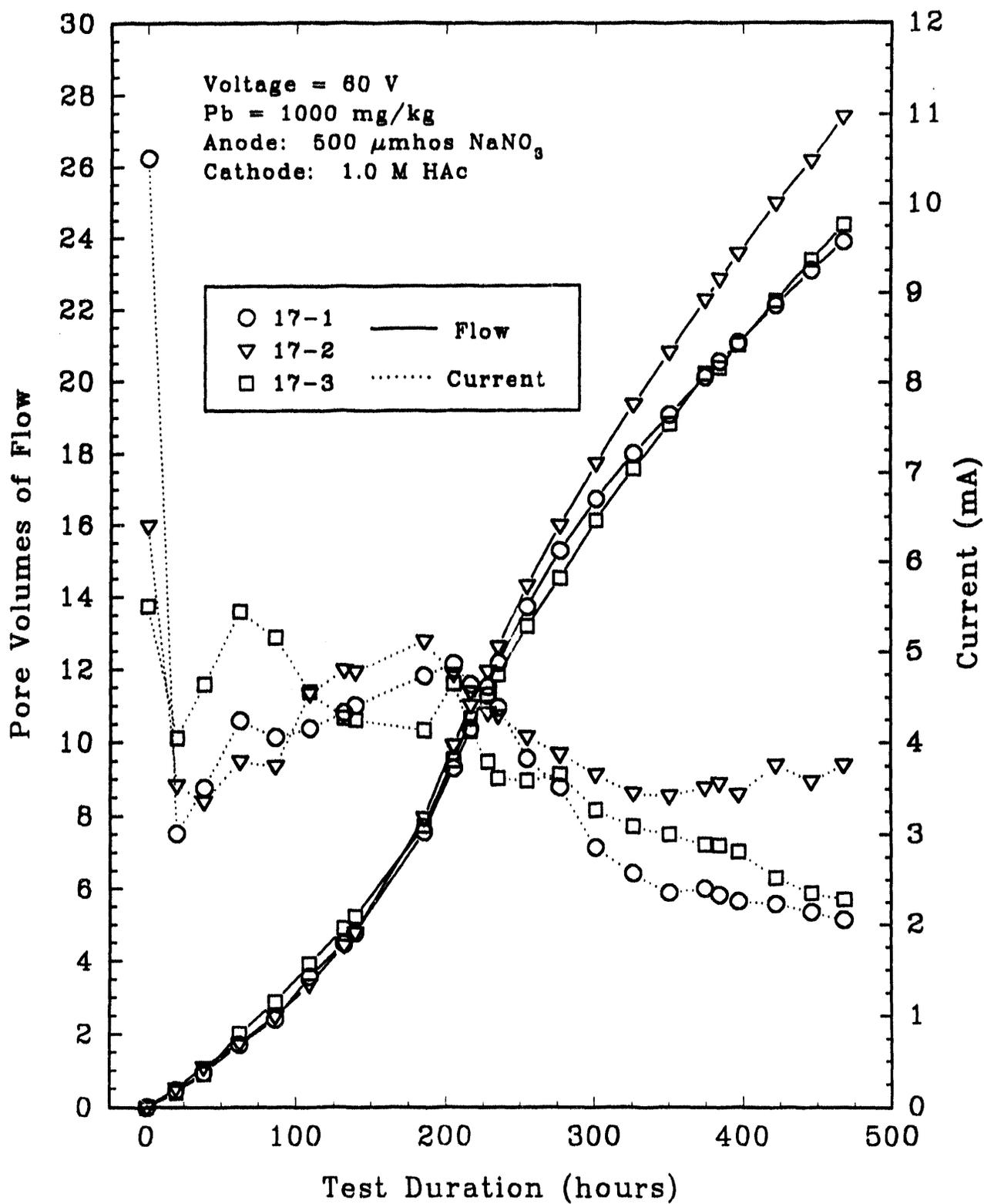


Figure 5.10. Volume of Water and Current as a Function of Time For Test 17

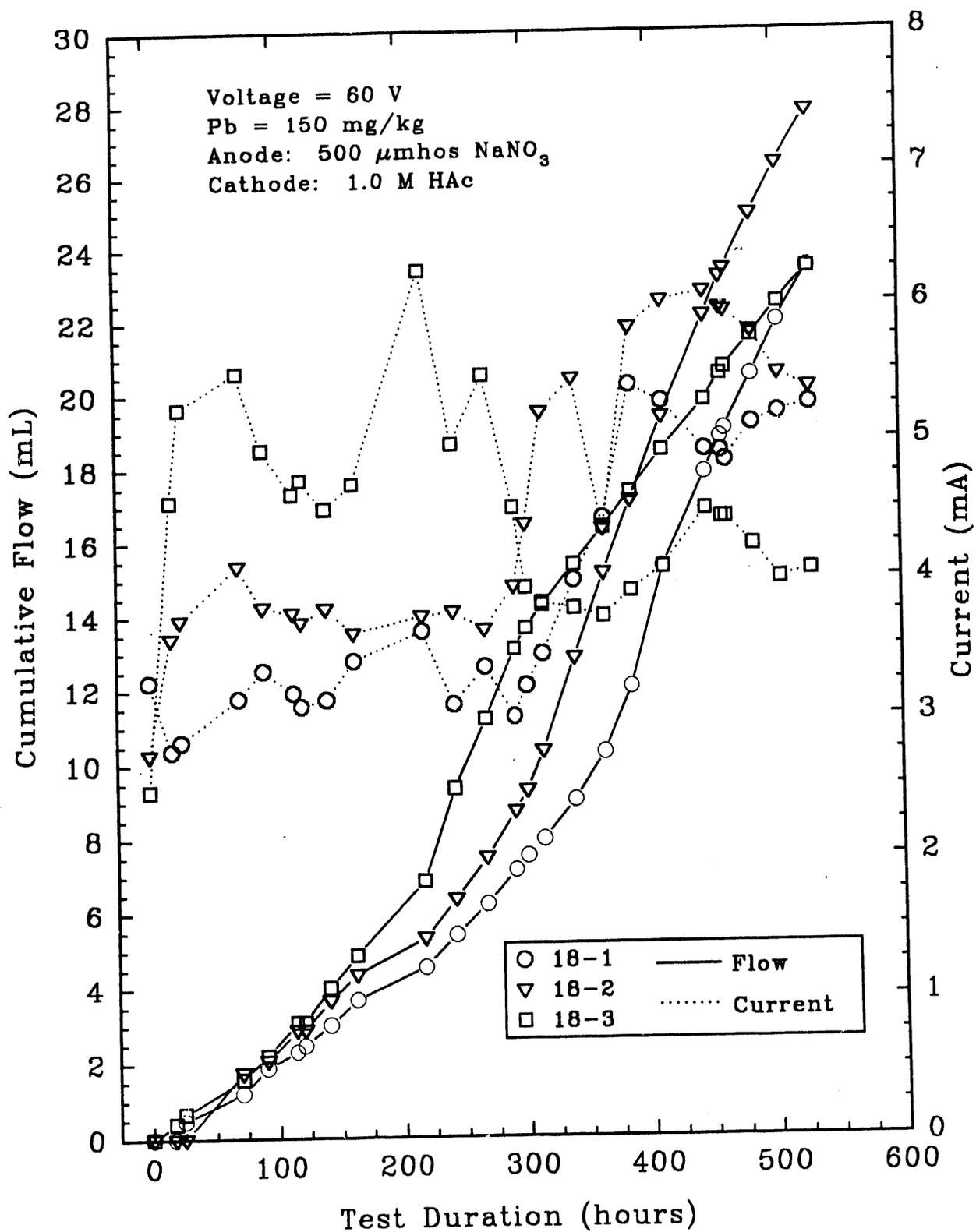


Figure 5.11: Volume of Water and Current as a Function of Time For Test 18

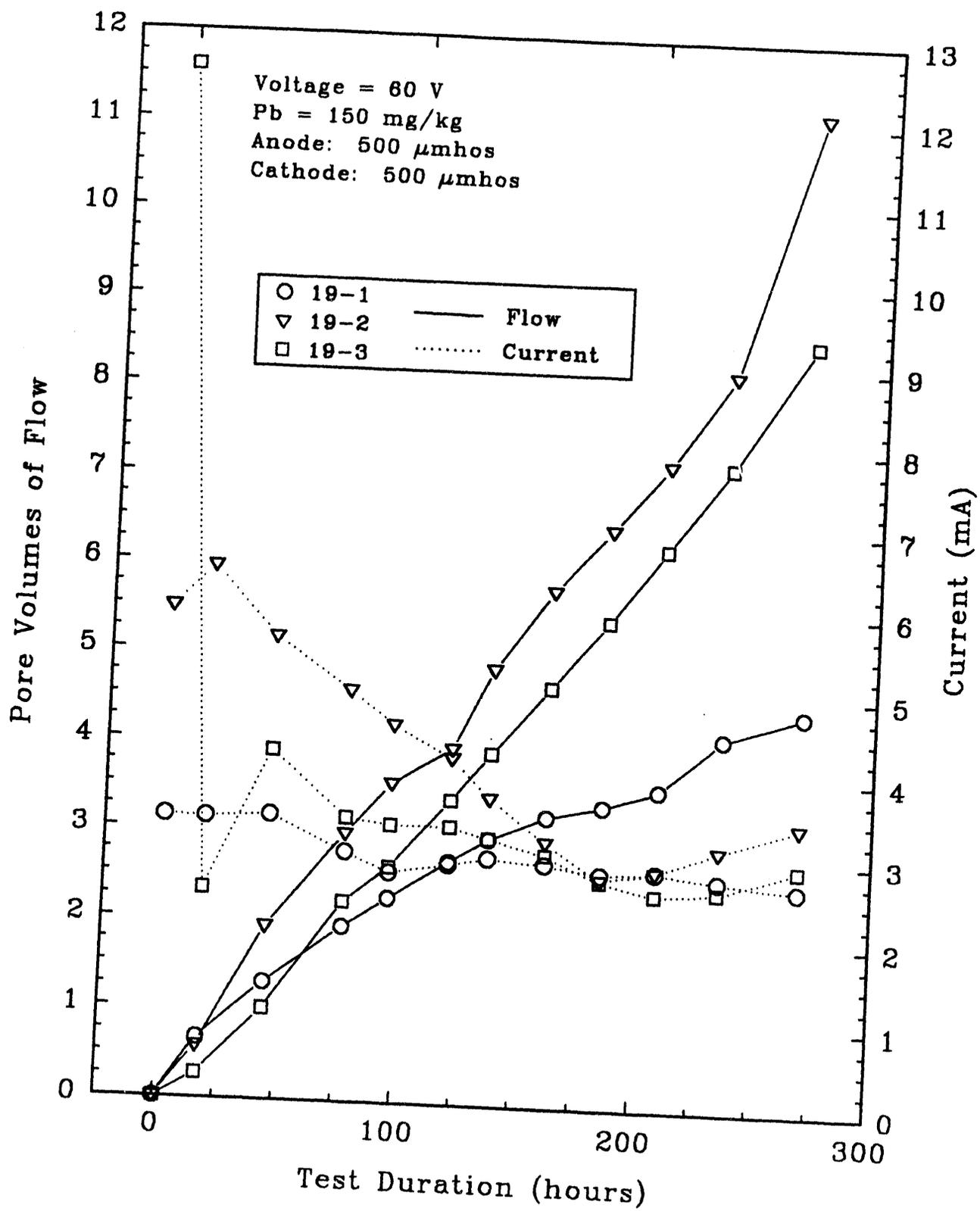


Figure 5.12. Volume of Water and Current as a Function of Time For Test 19

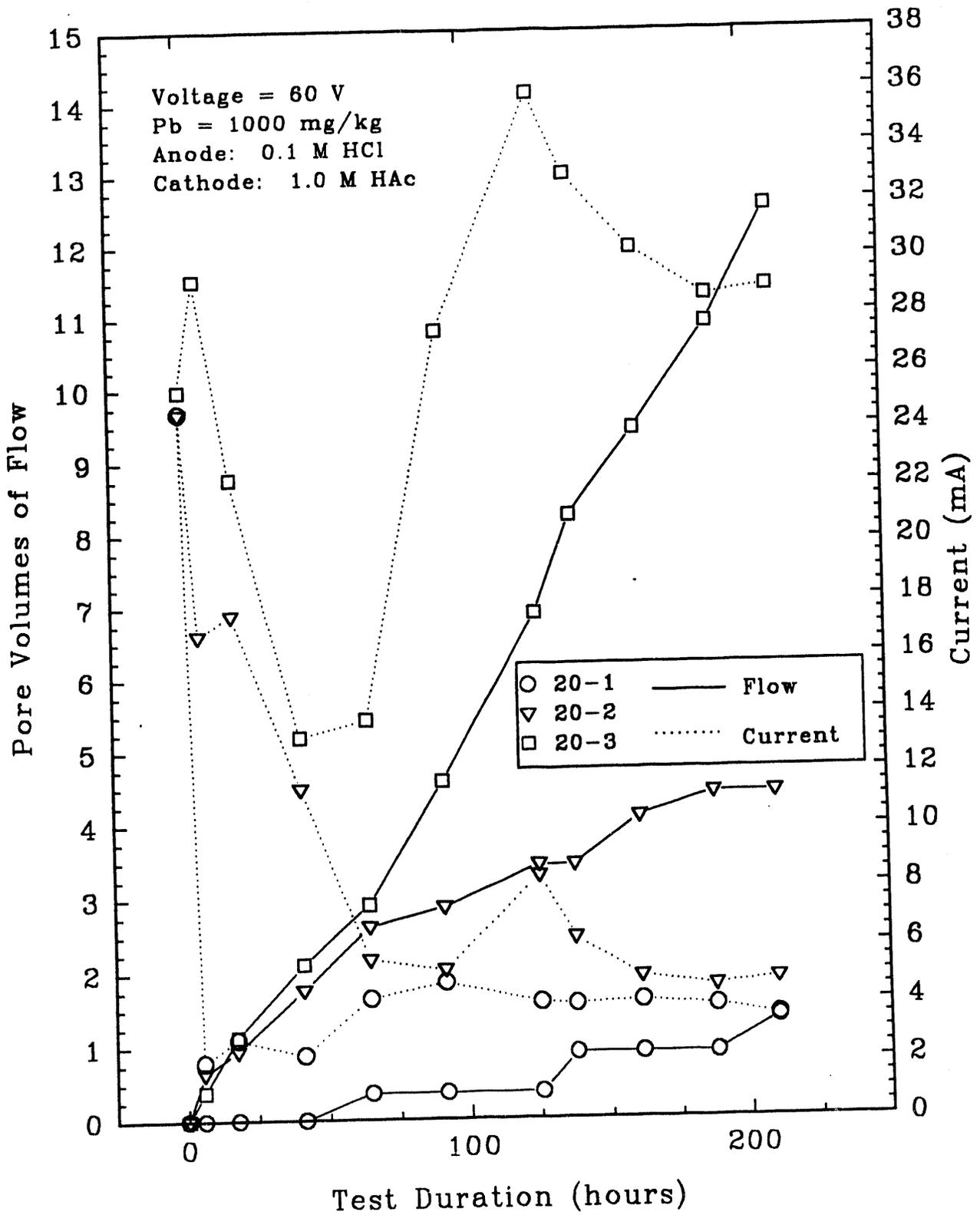


Figure 5.13. Volume of Water and Current as a Function of Time For Test 20

conducted with EDTA conditioning of the cathode reservoir produced zero flow thus, these experiments are not presented.

Flow rate and current results presented in Figures 5.4 through 5.13 were averaged over the duration of the experiment and for replicate tests and these data are presented in Table 5.4. The average flow rate, in pore volumes per day, represents the average flow rate for an individual test over the duration of the test. The mean flow rate represents an average of the triplicates (or duplicate) experiments. One standard deviation from the mean is also provided for the mean flow rate. Current data is also presented in a similar fashion. The coefficient of variation (standard deviation/mean) is provided as an indicator of the reproducibility of the experiments. In general, the level of reproducibility decreased as the ionic strength of the pore water (*i.e.*, initial lead concentration) decreased. A major exception to this observation was Test 20 where 0.1 N HCl was the anode conditioning agent. A possible reason for this phenomenon was poisoning of the cathode electrode with Pb from a previous experiment. In Tests 18, a large amount of Pb was transported into the cathode chamber where it was plated onto the electrode (as  $Pb^0$ ). Immediately following the completion of Test 18, Test 20 was setup using reactors from Test 18. The loss of Pb due to plating in Test 18 was not discovered until Test 20 was well underway (the Pb removal determination requires several days and because of time constraints the next set of experiments must be immediately placed on-line). In future work, electrodes will be acid rinsed to remove any lead that may have plated.

### 5.3.2 Effect of Initial Conditions on EO Water Movement and Current

In this section, the volume of water transported per day, the average current, the volume of soil water transported per amp-hour ( $K_j$ ), and the number of kW-hr required to pump one gallon are presented as a function of initial test conditions (*i.e.*, initial Pb contamination (soil water conductivity), reservoir conditioning, and applied voltage). The first parameter is important because for a contaminated soil to be efficiently remediated, soil water must be transported. As mentioned previously, EO water movement is one mechanism by which  $H^+$  is transported into the soil so that Pb (or other cationic heavy metals) desorption can occur. EO is also partly responsible for the transport of the released Pb into the cathode reservoir. Thus, the optimization of EO water movement is important. The latter quantities are used to estimate the efficiency of EO water movement from an economic standpoint.

Mean flow rates and currents as a function of initial soil Pb concentration and initial soil water conductivity are presented in Table 5.5. Also presented are the percent increases from the lowest flow rate and lowest current for tests that are comparable (*i.e.*, tests having similar initial conditions, *e.g.*, Test 11 and 13). Increasing the lead contamination level increased the soil water conductivity because  $NO_3^-$  is added with the lead during the contamination step (as  $PbNO_3$ ) and Pb displaces indigenous soil-bound cations. The initial soil water conductivities presented in Table 5.5 were determined using the soil water that was "squeezed" from the soil during the consolidation/contamination step. In all cases, both the flow rate and current increased when the initial lead concentration (and thus soil water conductivity) was increased. Since resistivity (resistance to  $e^-$  flow) is inversely proportional to conductivity, an increase in conductivity should

**Table 5.4. Average, Mean, and Coefficients of Variation for Flow Rates and Currents**

Test No.	Test Conditions <sup>1</sup>	Avg. Flow Rate <sup>2</sup> PV/d	Mean Flow Rate $\pm$ Std. <sup>3</sup>	Flow Rate CV <sup>4</sup>	Avg. Current <sup>5</sup> mA	Mean Current $\pm$ Std. <sup>6</sup>	Current CV <sup>7</sup>
11-1	1000/30/500/500	0.328	0.359 $\pm$ .094	0.26	1.59	2.00 $\pm$ 0.71	0.36
11-2		0.263			1.40		
11-3		0.487			3.00		
12-1	1000/30/DI/DI	0.144	0.141 $\pm$ 0.032	0.23	0.857	0.70 $\pm$ 0.13	0.19
12-2		0.178			0.540		
12-3		0.100			0.690		
13-1	150/30/500/500	0.149	0.171 $\pm$ 0.021	0.13	1.17	1.34 $\pm$ 0.16	0.12
13-2		0.193			1.50		
14-1	1000/30/DI/HAc	0.356	0.310 $\pm$ 0.047	0.15	1.11	1.15 $\pm$ .05	0.04
14-2		0.262			1.20		
15-1	1000/60/500/500	0.70	1.19 $\pm$ 0.35	0.30	2.68	3.83 $\pm$ 0.82	0.21
15-2		1.54			4.28		
15-3		1.33			4.53		
16-1	150/60/DI/HAc	0.245	0.256 $\pm$ 0.112	0.44	1.39	1.46 $\pm$ 0.39	0.27
16-2		0.399			1.97		
16-3		0.124			1.01		
17-1	1000/60/500/HAc	1.23	1.24 $\pm$ 0.080	0.06	3.59	3.80 $\pm$ 0.18	0.05
17-2		1.41			4.03		
17-3		1.25			3.78		
18-1	150/60/500/HAc	1.15	1.18 $\pm$ 0.071	0.06	3.97	4.36 $\pm$ 0.28	0.06
18-2		1.28			4.59		
18-3		1.11			4.52		
19-1	150/60/500/500	0.308	0.744 $\pm$ .310	0.41	2.54	3.11 $\pm$ 0.43	0.14
19-2		0.926			3.57		
19-3		0.999			3.21		
20-1	1000/60/HCl/HAc	0.154	0.700 $\pm$ 0.542	0.76	3.95	12.55 $\pm$	0.75
20-2		0.505			7.99		
20-3		1.44			25.7		

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

<sup>2</sup> Average Flow Rate Over the Entire Test Duration.

<sup>3</sup> Mean Flow Rate  $\pm$  One Standard Deviation For Replicates of Each Test.

<sup>4</sup> Flow Rate Coefficient of Variation (Standard Deviation/Mean).

<sup>5</sup> Average Current Over the Entire Test Duration.

<sup>6</sup> Mean Current  $\pm$  One Standard Deviation For Replicates of Each Test.

<sup>7</sup> Current Coefficient of Variation (Standard Deviation/Mean).

increase both current and flow. A continual increase in conductivity should eventually decrease flow because the EDL will be compressed, lowering the water/counter-ion ratio in the EDL. Buffering the cathode reservoir with acetic acid appears to limit the influence of soil water conductivity on flow.

**Table 5.5. Mean Flow Rate and Current as a Function of Initial Soil Pb Concentration and Initial Soil Water Conductivity**

Test No.	Test Conditions <sup>1</sup>	Soil Water Conductivity, $\mu\text{mho}$	Mean Flow Rate, PV/d	% Increase From Lowest Flow Rate	Mean Current, mAmp	% Increase From Lowest Current
11-1	1000/30/500/500	1410	0.359	110	2.00	50
11-2		1317				
11-3		1447				
13-1	150/30/500/500	$\approx 700$	0.171	----	1.34	---
13-2		$\approx 700$				
17-1	1000/60/500/HAc	2090	1.29	10	3.80	---
17-2		2050				
17-3		$\approx 2000$				
18-1	150/60/500/HAc	1020	1.18	----	4.36	15
18-2		809				
18-3		739				
15-1	1000/60/500/500	$\approx 1400$	1.19	61	3.83	23
15-2		$\approx 1400$				
15-3		$\approx 1400$				
19-1	150/60/500/500	655	0.74	----	3.11	---
19-2		696				
19-3		652				

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

Mean flow rates and currents as a function of reservoir conditioning are presented in Table 5.6. Also presented are the percent increase from the lowest flow rate and lowest current for tests that are comparable. For Tests 11, 12, and 14, an increase in the reservoirs' conductivity increased both flow and current. Buffering the cathode reservoirs with either  $\text{NaNO}_3$  or HAc while conditioning the anode reservoir with  $\text{NaNO}_3$  produced the highest flow rates.

Mean flow rates and currents as a function of applied voltage are presented in Table 5.7. Voltage had the largest influence on both the flow rate and current. Increasing the voltage from 30 to 60 V produced a 230 to 330 percent increase in flow and between a 90 and 230 percent increase in current. Increasing the voltage did not cause a noticeable increase in soil temperature or cause

further soil consolidation. In future work, larger voltages will be investigated to determine if an optimum voltage exists. It should be noted that increasing the current will increase power consumption (and operating costs). In subsequent paragraphs the amount of water pumped per amp-hr and the kW-hr required to pump one gallon of soil water are presented.

**Table 5.6. Mean Flow Rate and Current as a Function of Reservoir Conditioning**

Test No.	Test Conditions <sup>1</sup>	Mean Flow Rate, PV/d	% Increase From Lowest Flow Rate	Mean Current, mAmp	% Increase From Lowest Current
11	1000/30/500/500	0.359	155	2.00	185
12	1000/30/DI/DI	0.141	----	0.70	---
14	1000/30/DI/500	0.310	120	1.15	65
15	1000/60/500/500	1.19	70	3.83	---
17	1000/60/500/HAc	1.29	84	3.80	1
20	1000/60/HCl/HAc	0.70	----	12.6	230
16	150/60/DI/HAc	0.256	----	1.46	---
18	150/60/500/HAc	1.18	360	4.36	200
19	150/60/500/500	0.74	190	3.11	115

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

**Table 5.7. Mean Flow Rate and Current as a Function Applied Voltage**

Test No.	Test Conditions <sup>1</sup>	Mean Flow Rate, PV/d	% Increase From Lowest Flow Rate	Mean Current, mAmp	% Increase From Lowest Current
11	1000/30/500/500	0.359	----	2.00	---
15	1000/60/500/500	1.19	231	3.83	90
13	150/30/500/500	0.171	----	1.34	---
19	150/60/500/500	0.74	330	3.11	130
14	1000/30/DI/HAc	0.310	----	1.15	---
17	1000/60/500/HAc	1.29	315	3.80	230

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

In Table 5.8, the average and mean values for the coefficient of water-transport efficiency ( $K_i$ ) and the total energy output per gallon of soil water pumped ( $E_T$ ) are presented. Also included in Table 5.8 are the coefficients of variation for the mean values of  $K_i$  and  $E_T$ .  $K_i$  and  $E_T$  are measures of how efficient water is transported under an applied voltage.  $E_T$  can be used to compare power costs required for pumping between different operating conditions. A larger  $K_i$  and a smaller  $E_T$  correspond to more efficient water movement.  $K_i$  was determined by dividing the total amount of

soil water pumped by the area under the current-time curve (amp-hr, see Figures 5.4 through 5.13).  $E_T$  was calculated by multiplying the total amp-hr by the applied voltage and dividing by the gallons of soil water pumped.

**Table 5.8 Average and Mean Values for the Coefficient of Water-Transport Efficiency ( $K_i$ ) and Total Energy Output ( $E_T$ )**

Test No.	Test Conditions <sup>1</sup>	Avg $K_i$ <sup>2</sup> mL/amp-hr	Mean $K_i$ $\pm$ Std. <sup>3</sup> (CV)	Avg. $E_T$ <sup>4</sup> kW-hr/gal	Mean $E_T$ $\pm$ Std. <sup>5</sup> (CV) <sup>6</sup>
11-1	1000/30/500/500	266	240 $\pm$ 21 (0.09)	0.427	0.477 $\pm$ 0.042 (0.09)
11-2		240		0.473	
11-3		214		0.529	
12-1	1000/30/DI/DI	218	279 $\pm$ 107 (0.38)	0.520	0.459 $\pm$ 0.141 (0.31)
12-2		429		0.264	
12-3		191		0.594	
13-1	150/30/500/500	167	165 $\pm$ 2	0.679	0.685 $\pm$ 0.01 (0.01)
13-2		164		0.691	
14-1	1000/30/DI/HAc	433	367 $\pm$ 66 (0.18)	0.262	0.319 $\pm$ 0.057 (0.18)
14-2		301		0.377	
15-1	1000/60/500/500	333	391 $\pm$ 54 (0.14)	0.682	0.592 $\pm$ 0.079 (0.13)
15-2		463		0.490	
15-3		376		0.603	
16-1	150/60/DI/HAc	221	215 $\pm$ 43 (0.20)	1.03	1.10 $\pm$ 0.24 (0.22)
16-2		264		0.858	
16-3		158		1.43	
17-1	1000/60/500/HAc	440	438 $\pm$ 9 (0.02)	0.515	0.518 $\pm$ 0.011 (0.02)
17-2		449		0.505	
17-3		429		0.532	
18-1	150/60/500/HAc	378	347 $\pm$ 28 (0.08)	0.600	0.658 $\pm$ 0.054 (0.08)
18-2		352		0.643	
18-3		311		0.730	
19-1	150/60/500/500	151	290 $\pm$ 100 (.35)	1.50	0.923 $\pm$ 0.411 (0.45)
19-2		336		0.676	
19-3		384		0.591	
20-1	1000/60/HCl/HAc	49	68 $\pm$ 13 (0.20)	4.59	3.50 $\pm$ 0.79 (0.22)
20-2		81		2.79	
20-3		72		3.13	

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

<sup>2</sup> Average  $K_i$  For Individual Test.

<sup>3</sup> Mean  $K_i$   $\pm$  One Standard Deviation (Std) For Replicates of Each Test.

<sup>4</sup> Average  $E_T$  For Individual Test.

<sup>5</sup> Mean  $E_T$   $\pm$  One Standard Deviation (Std) For Replicates of Each Test.

<sup>6</sup> Coefficient of Variation (Std/Mean)

For all cases, the standard deviation from the mean and the coefficients of variation for  $K_i$  and  $E_T$  were smaller than those observed for the flow rate and current because the dependence of flow on current is taken into account when calculating  $K_i$  and  $E_T$ . Thus, determining the effect of initial conditions on EO flow may be more reliable if  $K_i$  and  $E_T$  are used. What is not accounted for in Table 5.8 is the possibility that for long test durations, flow cessation may occur for some operating conditions. This phenomenon was discussed earlier when Figures 5.4 through 5.13 were presented. For the experiments reported herein, flow cessation did not occur, but for some tests, flow began to decrease with time (Tests 12, 13, 20). When designing a EK soil flushing system, altering operating conditions so that flow cessation does not occur may be required.

As with flow and current, the effect of lead concentration and initial soil conductivity, reservoir conditioning, and applied voltage on  $K_i$  and  $E_T$  is discussed individually. In the discussion that follows, general statements alluding to the costs associated with EK soil flushing are made. These observations do not take the place of a detailed economic analysis.

In Table 5.9, mean values of  $K_i$  and  $E_T$  as functions of initial soil Pb concentration (soil water conductivity) are presented. At higher soil Pb concentrations (soil water conductivity), EO flow was more efficient (larger  $K_i$  and smaller  $E_T$  for 1000 mg/kg Pb (1400-2000  $\mu\text{mho}$ ) compared with 150 mg/kg Pb (650-850  $\mu\text{mho}$ )). As was mentioned previously, this observation is in conflict with accepted theory (Hamad *et al* 1991, and Gray and Mitchell 1967) that predicts lower EO flow as pore water conductivity increases. However, Gray and Mitchell (1967) used short-term electrophoresis data, not EO flow data to validate their model. Further research on the relationship between EO flow and soil water conductivity is required if the EK soil flushing process is to be correctly modeled and applied to actual sites. The results in Table 5.9 indicate that soils with higher levels of contamination may be more easily remediated because it is easier to "flush" the soil (Note, this observation neglects the attraction of the lead for the soil surface).

**Table 5.9. Mean  $K_i$  and  $E_T$  as a Function of Initial Soil Pb Concentration and Initial Soil Water Conductivity**

Test No.	Test Conditions <sup>1</sup>	Soil Water Conductivity, $\mu\text{mho}$	Mean $K_i$ , mL/amp-hr	Mean $E_T$ , kW-hr/gal.
11	1000/30/500/500	$\approx 1400$	240	0.477
13	150/30/500/500	$\approx 700$	165	0.685
17	1000/60/500/HAc	$\approx 2000$	438	0.518
18	150/60/500A/HA	$\approx 850$	347	0.658
15	1000/60/500/500	$\approx 1400$	391	0.592
19	150/60/500/500	$\approx 650$	290	0.923

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

In Table 5.10 mean values of  $K_i$  and  $E_T$  as a function of reservoir conditioning are presented. Reservoir conditioning had a less noticeable effect on  $K_i$  and  $E_T$  compared to initial Pb

contamination (soil water conductivity). An exception was Test 20, where 0.1 N HCl used to condition the anode. Test 20 had much lower  $K_i$  and much higher  $E_T$  compared to the other Tests. During Test 20,  $Cl_2$  (g) was detected olfactory. The production of  $Cl_2$  (g) from  $Cl^-$  requires energy thus  $Cl_2$  formation could significantly affect  $K_i$  and  $E_T$ . The production of  $Cl_2$  (g) could also present a health and safety problem.

**Table 5.10. Mean  $K_i$  and  $E_T$  as a Function of Reservoir Conditioning**

Test No.	Test Conditions <sup>1</sup>	Mean $K_i$ , mL/amp-hr	Mean $E_T$ , kW-hr/gal.
11	1000/30/500/500	240	0.477
12	1000/30/DI/DI	279	0.460
14	1000/30/DI/500	367	0.319
15	1000/60/500/500	391	0.592
17	1000/60/500/HAc	438	0.518
20	1000/60/HCl/HAc	68	3.50
16	150/60/DI/HAc	215	1.10
18	150/60/500/HAc	347	0.658
19	150/60/500/500	290	0.923

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition  
(See Table 4.3).

In Table 5.11 mean values of  $K_i$  and  $E_T$  as a function of applied voltage are presented. Increasing the voltage increased the volume of water transported per amp-hr ( $K_i$ ) but increased the power required per gallon ( $E_T$ ). Note, the increase in power costs may be offset by a decrease in other costs (personnel, monitoring, *etc*) resulting from a decrease in time required to remediate the site.

**Table 5.11. Mean  $K_i$  and  $E_T$  as a Function Applied Voltage**

Test No.	Test Conditions <sup>1</sup>	Mean $K_i$ , mL/amp-hr	Mean $E_T$ , kW-hr/gal.
11	1000/30/500/500	240	0.477
15	1000/60/500/500	390	0.592
13	150/30/500/500	165	0.685
19	150/60/500/500	290	0.923
14	1000/30/DI/HAc	367	0.319
17	1000/60/500/HAc	438	0.518

<sup>1</sup> Pb concentration Voltage/Anode Condition/Cathode Condition  
(See Table 4.3)

### 5.3.3 Soil pH and Soil Pb Concentration Under EK Soil Flushing

In Figures 5.14 through 5.23, soil lead concentrations and soil pHs are presented as a function normalized distance from the anode for Tests 11 through 20, respectively. In Table 5.12, the percent of the soil (by weight) that had greater than 50, 80, and 95 percent of the soil-bound lead removed are presented. Also included in Table 5.12 are the PVs of soil water transported and the test duration.

**Table 5.12 Percent Soil by Weight with Greater than 50, 80, and 95 Percent Pb Removal**

Test No.	Test Condition <sup>1</sup>	PV <sup>2</sup> (Duration)	% Soil (by weight) With > X % Pb Removal (Individual Test and Mean $\pm$ Std)					
			X=50		X = 80		X = 95	
11-1	1000/30/500/500	2.3 (169)	13		0		0	
11-2		2.1 (188)	11	16 $\pm$ 6	0	4 $\pm$ 6	0	0
11-3		2.9 (143)	24			12		0
12-1	1000/30/DI/DI	4.0 (672)	29		17		0	
12-2		5.0 (672)	28	27 $\pm$ 2	0	10 $\pm$ 7	0	0
12-3		2.7 (654)	23			13		0
13-1	150/30/500/500	3.9 (619)	0	0	0	0	0	0
13-2		5.0 (619)	0			0		0
14-1	1000/30/DI/HAc	11.1 (747)	58	54 $\pm$ 5	33	35 $\pm$ 2	0	0
14-2		8.2 (747)	49			37		0
15-1	1000/60/500/500	7.8 (267)	36		23		0	
15-2		17.3 (267)	51	50 $\pm$ 5	37	28 $\pm$ 7	0	0
15-3		14.9 (267)	62			24		0
16-1	150/60/DI/HAc	1.9 (188)	0		0		0	
16-2		3.1 (188)	0	0	0	0	0	0
16-3		1.0 (188)	0			0		0
17-1	1000/60/500/HAc	22.2 (421)	86		49		0	
17-2		25.0 (421)	100	91 $\pm$ 6	62	54 $\pm$ 6	0	0
17-3		22.2 (421)	87			50		0
18-1	150/60/500/HAc	25.0 (524)	60		10		0	
18-2		27.9 (524)	73	64 $\pm$ 6	0	11 $\pm$ 9	0	0
18-3		24.3 (524)	59			23		0
19-1	150/60/500/500	5.7 (448)	10		0		0	
19-2		17.3 (448)	23	19 $\pm$ 6	0	4 $\pm$ 5	0	0
19-3		18.6 (448)	23			11		0
20-1	1000/60/HCl/HAc	1.3 (210)	54		28		0	
20-2		4.4 (210)	100	85 $\pm$ 22	62	63 $\pm$ 30	34	26 $\pm$ 19
20-3		12.6 (210)	100			100		45

<sup>1</sup> Pb concentration/Voltage/Anode Condition/Cathode Condition (See Table 4.3).

<sup>2</sup> Pore Volumes of Water Transported for Given Test Duration (hours).

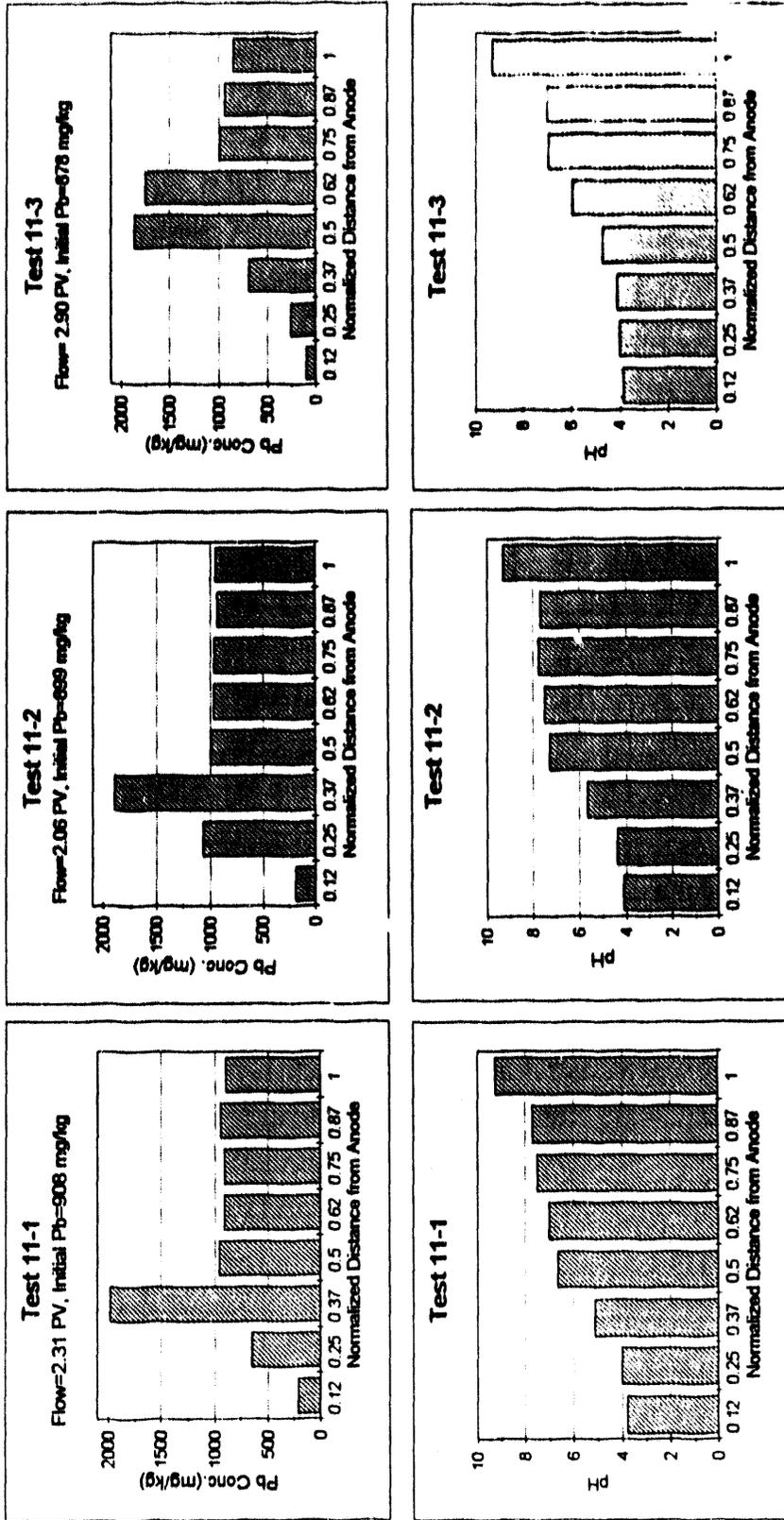


Figure 5.14. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 11 (Test Condition Identifier: 1000/30/500/500)

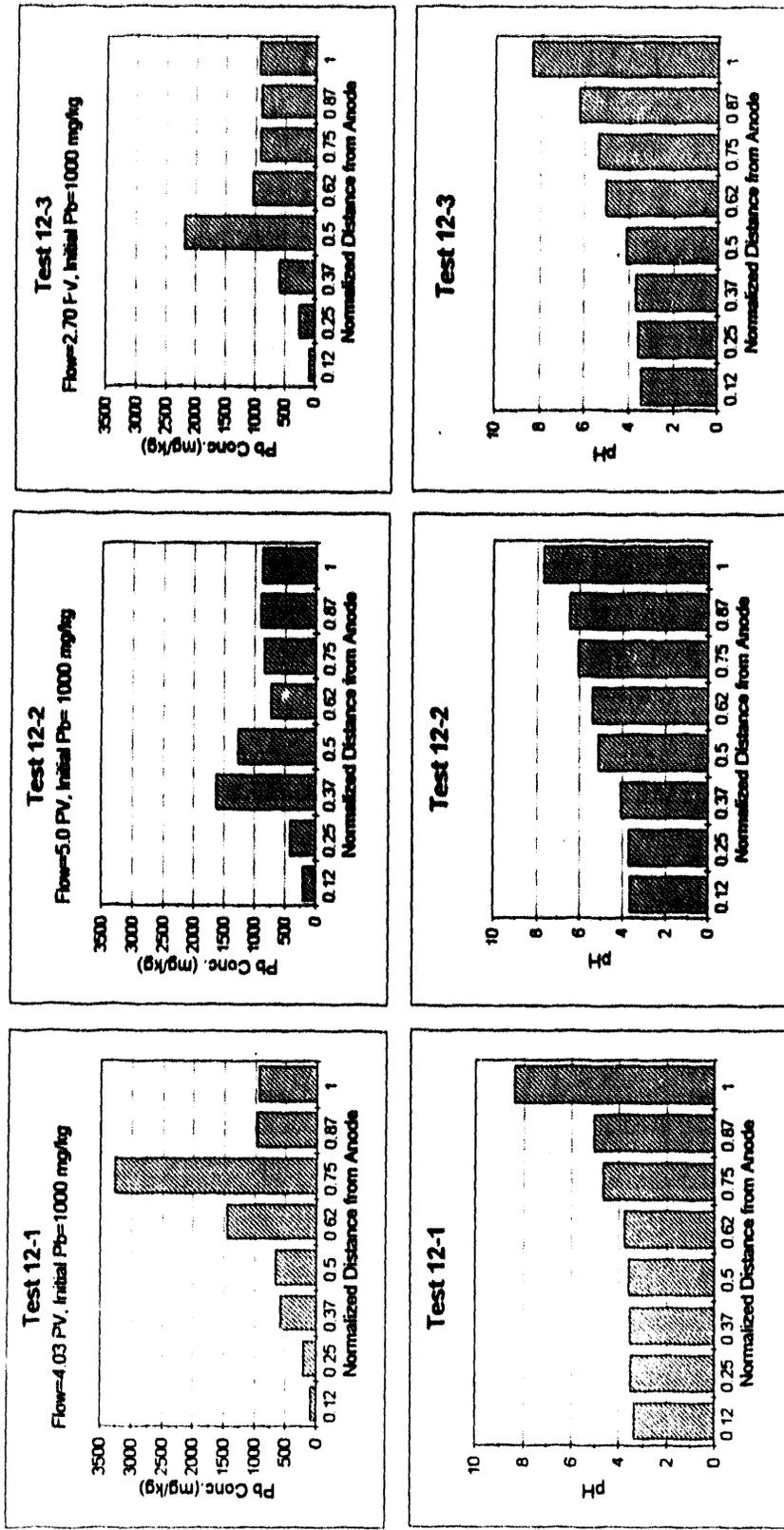


Figure 5.15. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 12 (Test Condition Identifier: 1000/30/DI/DI)

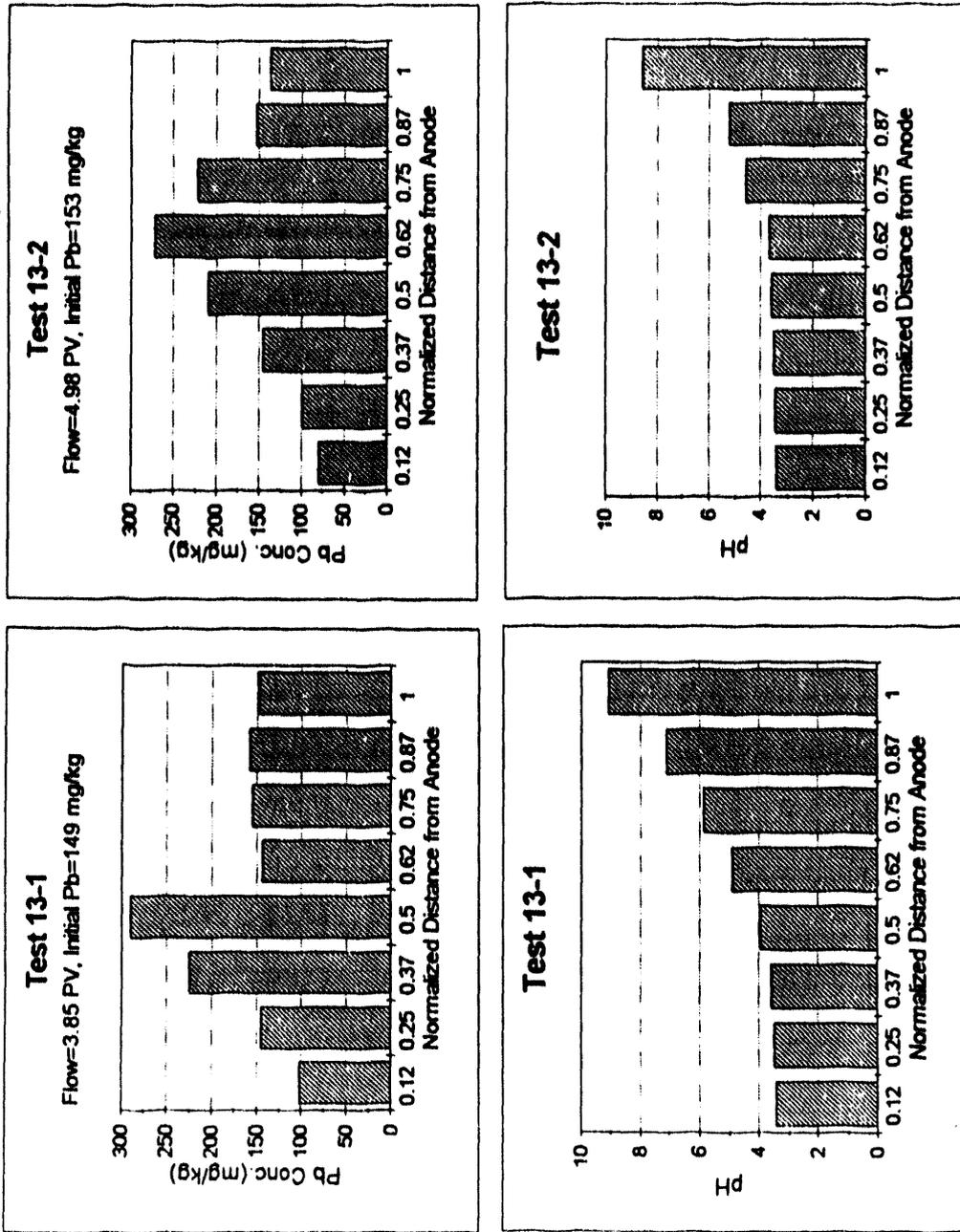


Figure 5.16. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 13 (Test Condition Identifier: 150/30/500/500)

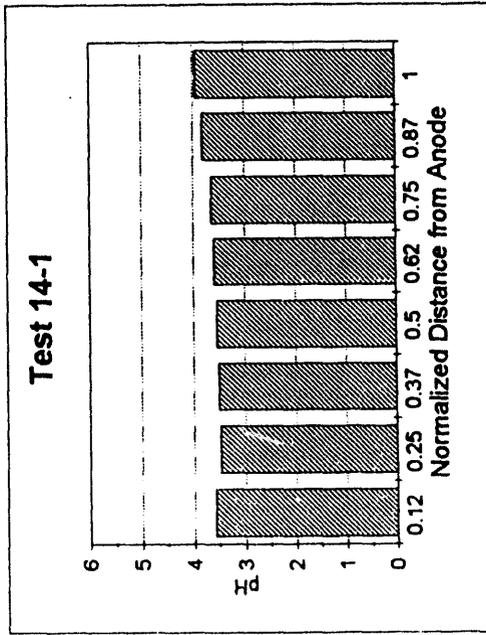
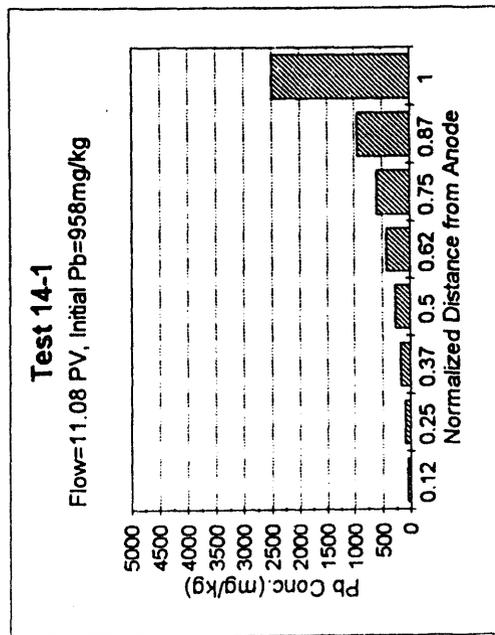
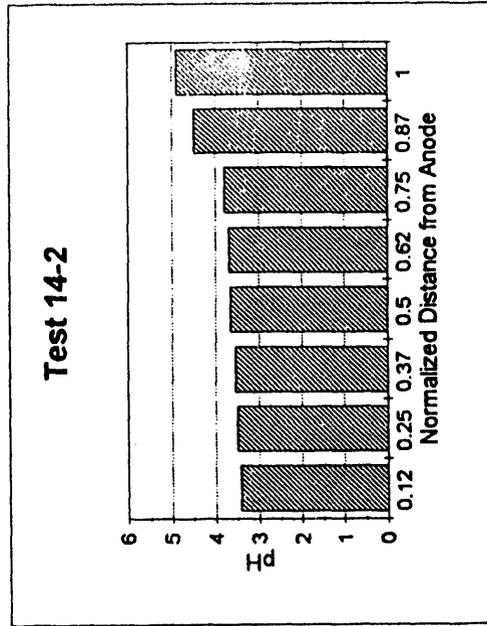
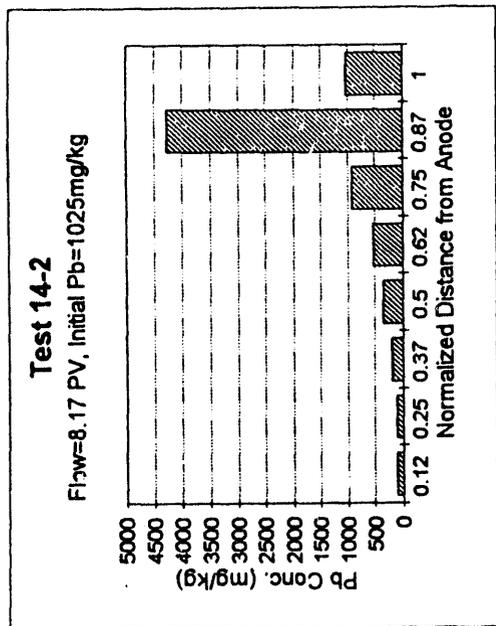


Figure 5.17. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 14 (Test Condition Identifier: 1000/30/DI/HAc)

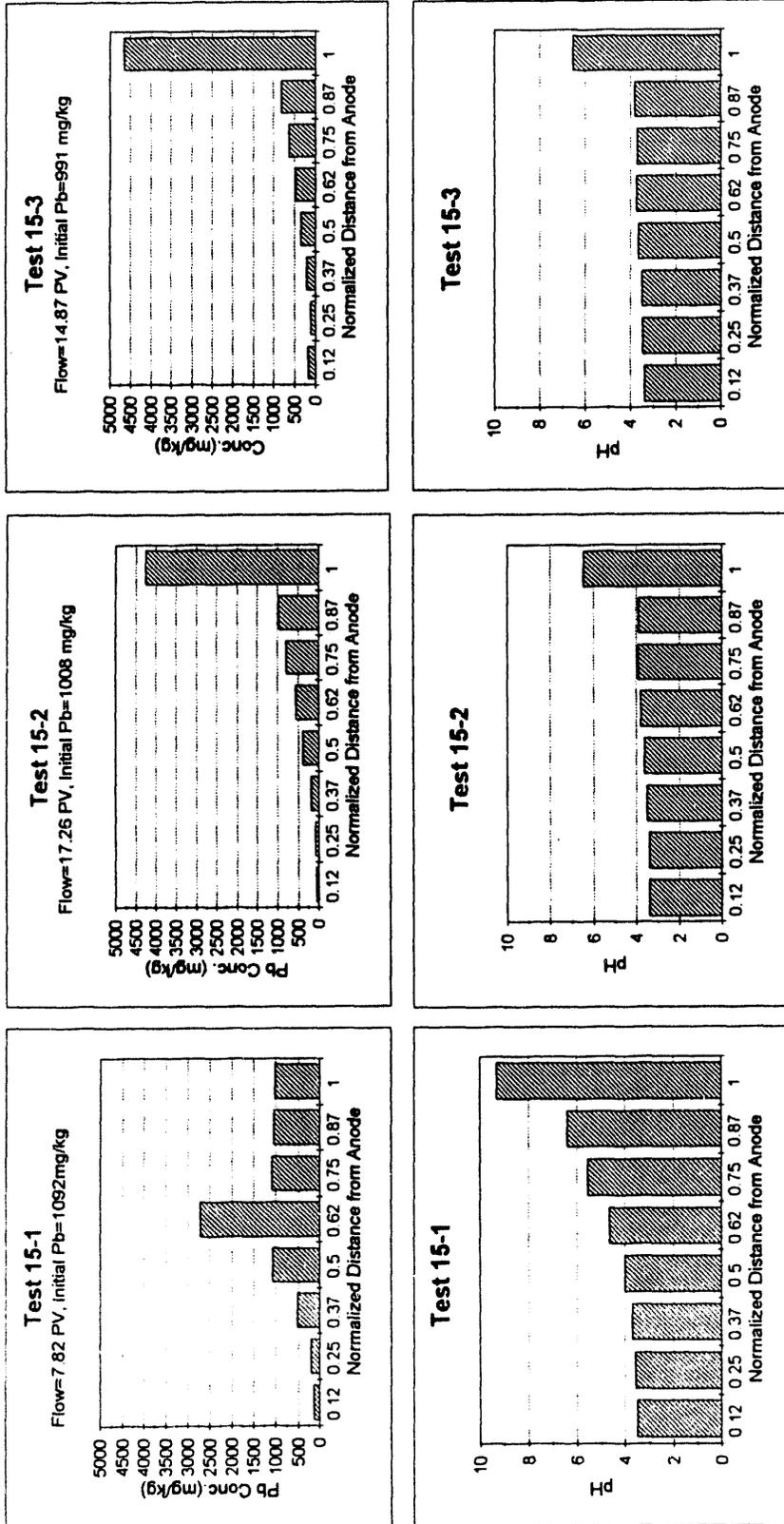


Figure 5.18. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 15 (Test Condition Identifier: 1000/60/500/500)

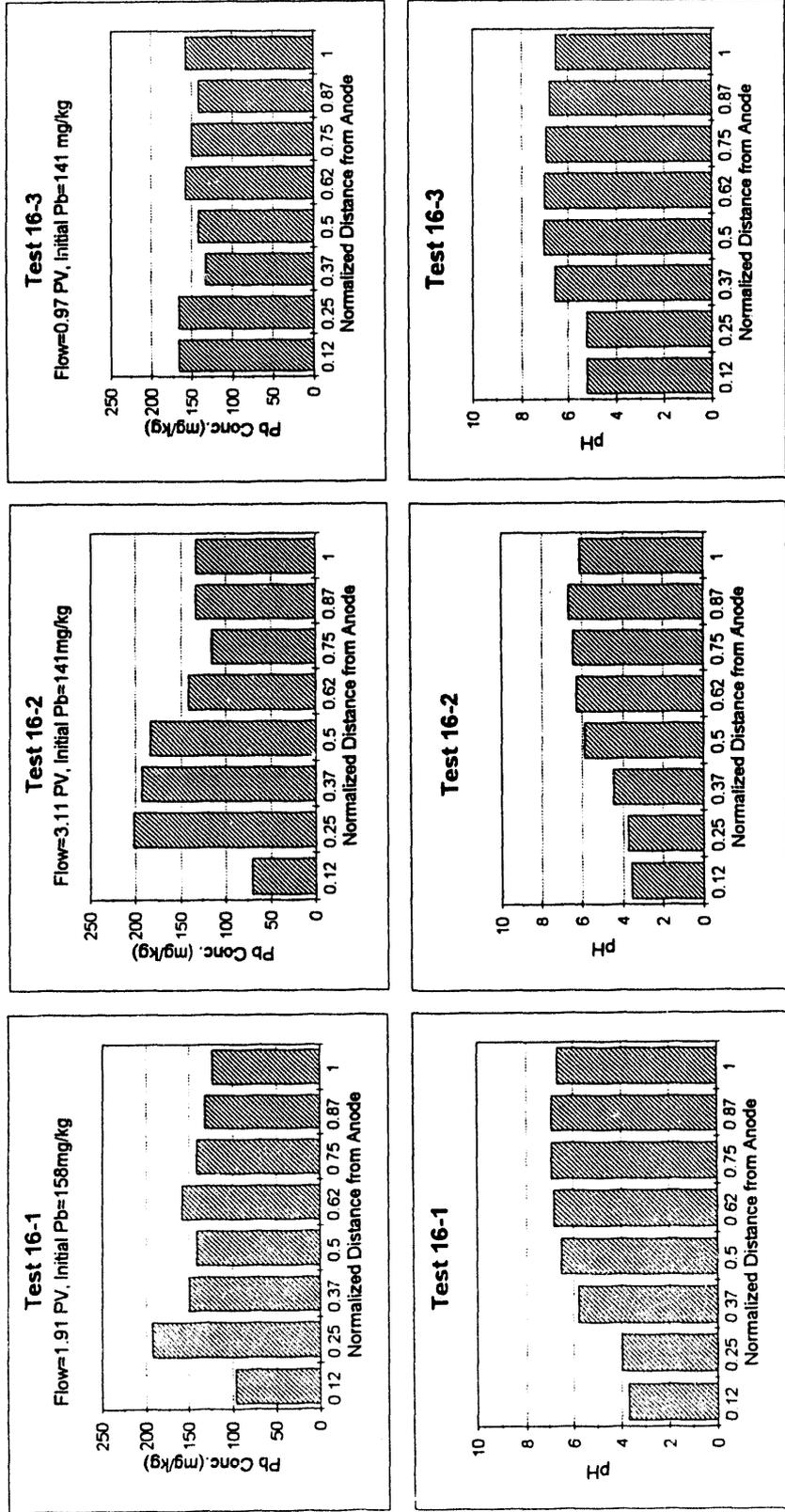


Figure 5.19. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 16 (Test Condition Identifier: 150/60/DI/HAc)

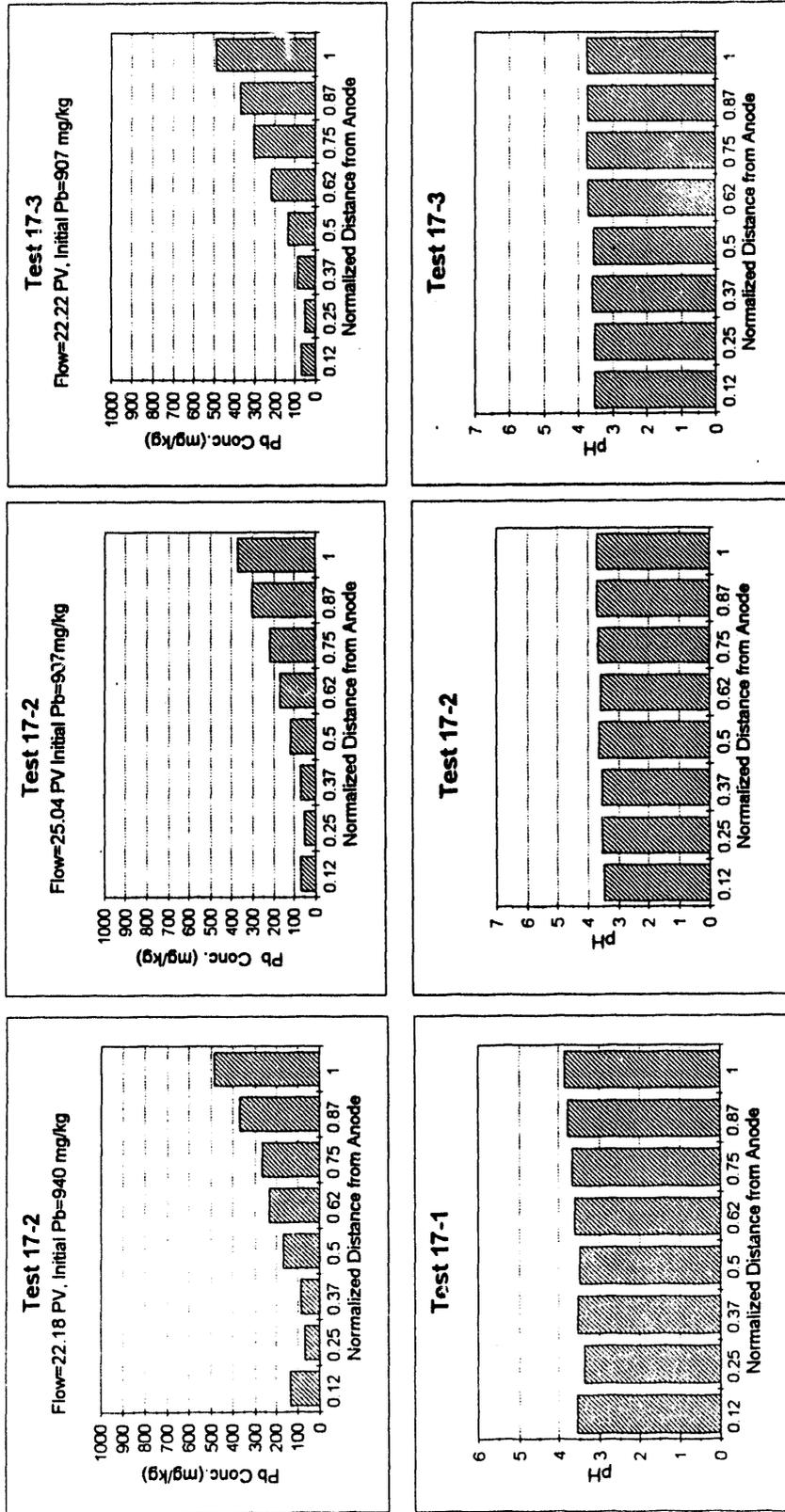


Figure 5.20. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 17 (Test Condition Identifier: 1000/60/500/HAC)

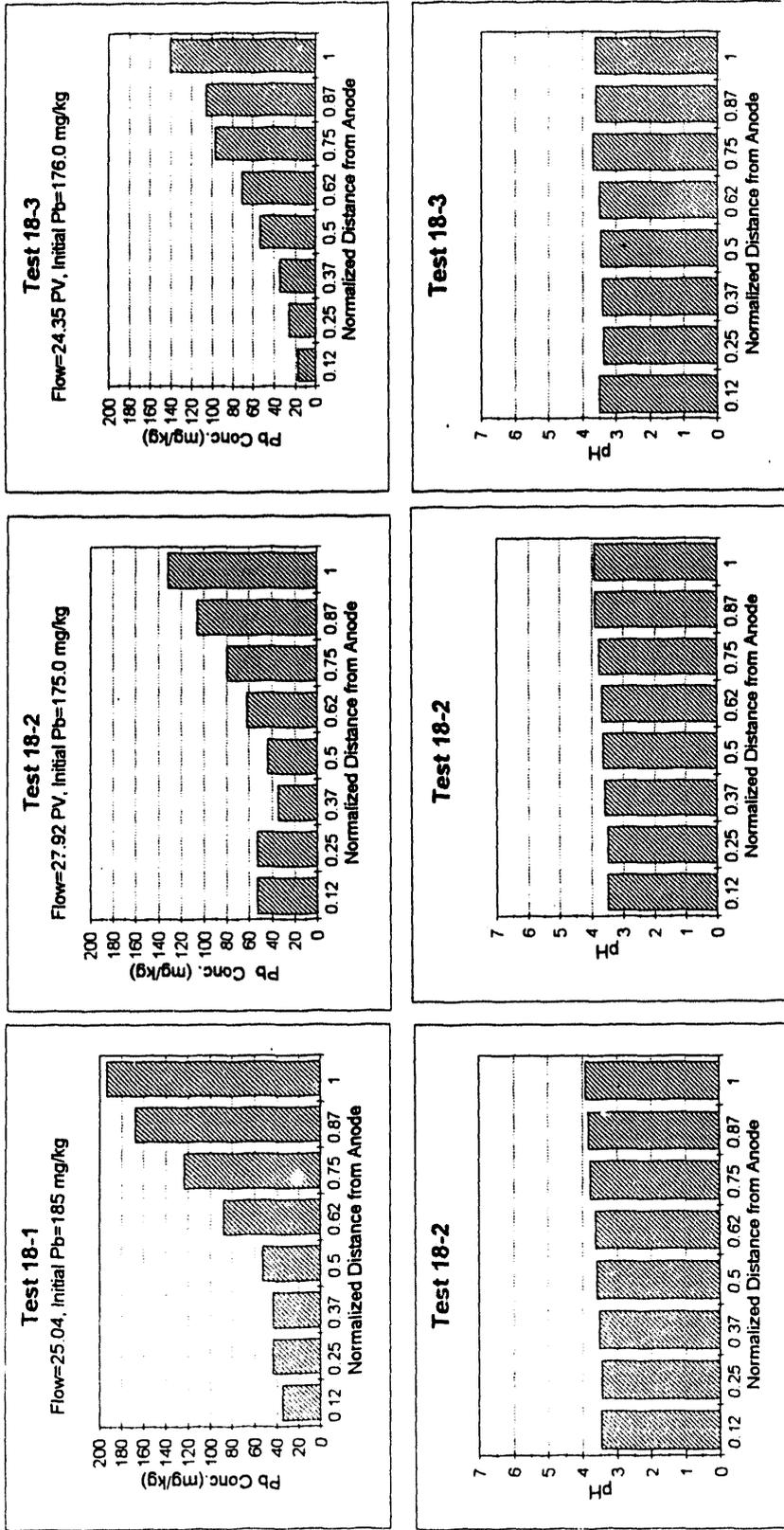


Figure 5.21. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 18 (Test Condition Identifier: 150/60/500/HAc)

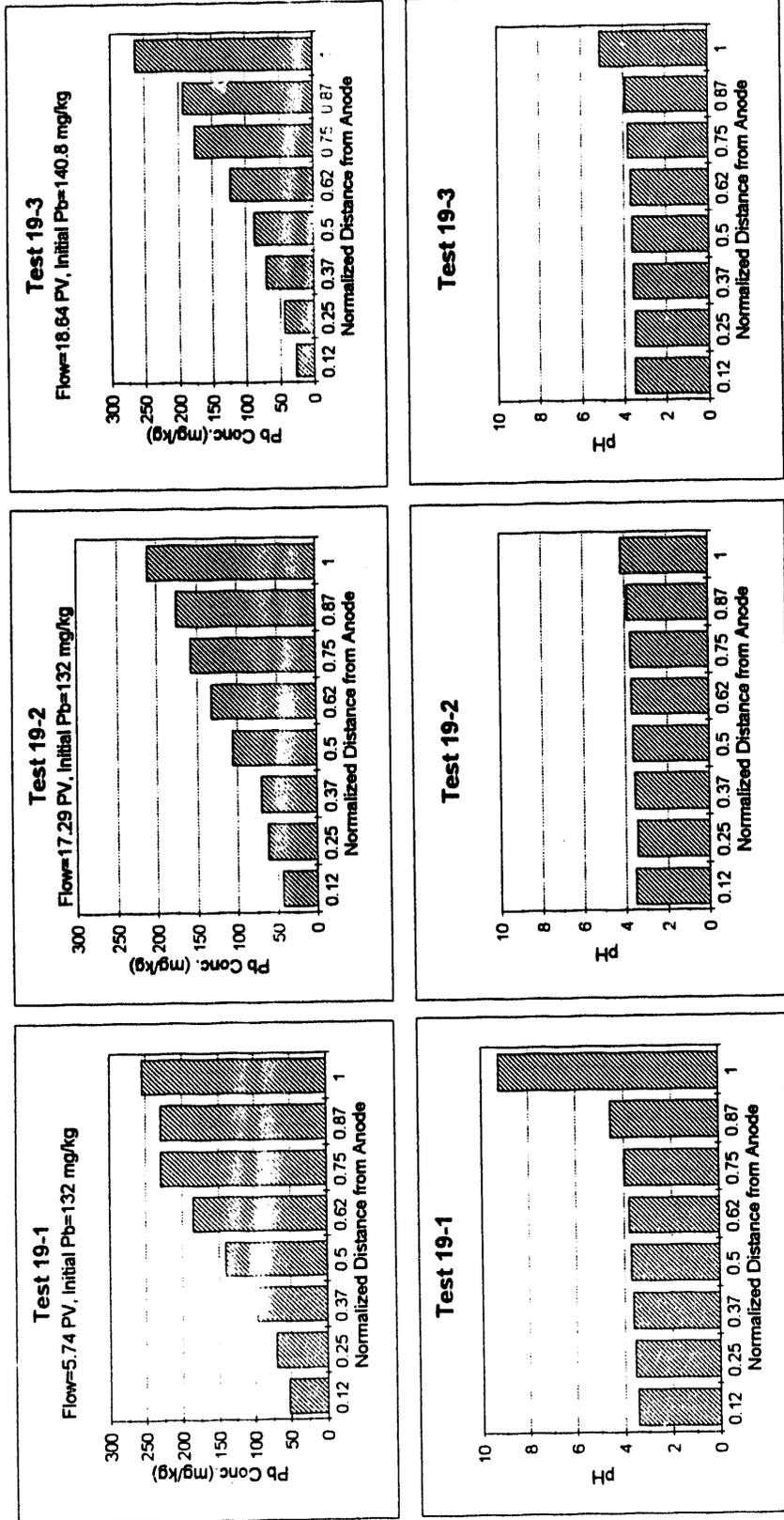


Figure 5.22. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 19 (Test Condition Identifier: 150/60/500/500)

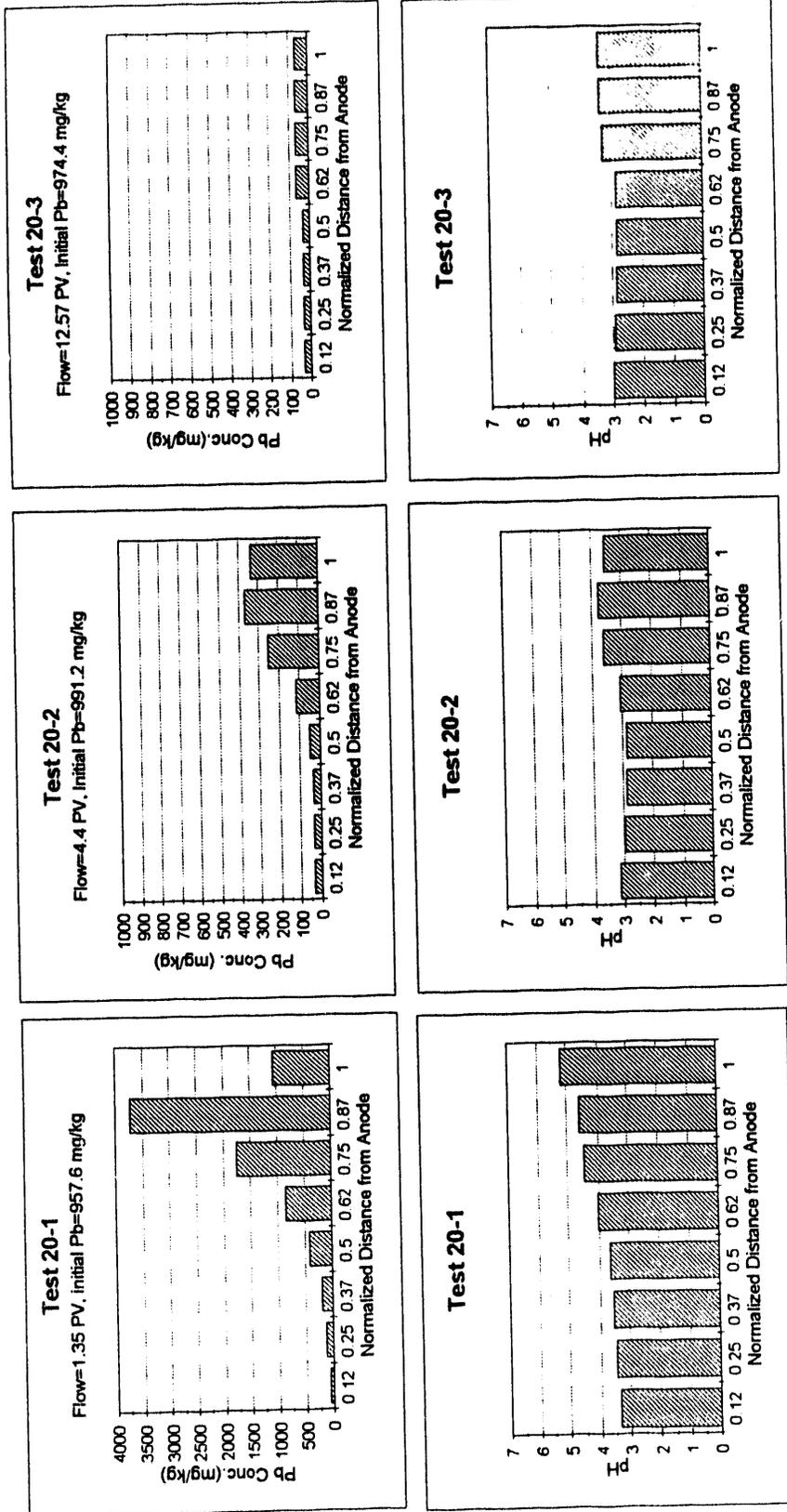


Figure 5.23. Soil Lead Concentration and Soil pH Versus Normalized Distance From the Anode for Test 20 (Test Condition Identifier: 1000/60/HCl/HAc)

Based on the data in Figures 5.14 through 5.23 and Table 5.12, the following observations can be made regarding the performance of EK soil flushing:

1.) For tests that did not have cathode reservoir pH control (Tests 11, 12, 13, 15, and 19) the pH of the soil segment next to the cathode was higher than the initial pH ( $\text{pH} \approx 8.5$  to 9 compared with  $\text{pH}_{\text{initial}} \approx 6.5$ ). The  $\text{OH}^-$  produced from electrolysis of water in the cathode was transported in the direction opposite of advection by diffusion and ion migration. The  $\text{OH}^-$  that is transported into the soil will precipitate with the desorbed lead and increase the likelihood of adsorption (adsorption increases with increasing pH). Thus, the overall remediation efficiency is decreased. Tests 15-2, 15-3, 19-2, and 19-3 were an exception to this observation. In these tests, there was sufficient transport of  $\text{H}^+$  to lower the soil pH at the cathode. For these tests, 15 or more pore volumes of water were transported.

2.) The lead that was desorbed from the soil nearest the anode was transported towards the cathode where it either resided in the pore liquid in aqueous form, adsorbed back onto the soil, or was precipitated. Based on the soil pHs for the segments that had Pb concentrations greater than the initial levels (either 150 or 1000 mg/kg), lead was precipitated (in the pore liquid or on the soil surface) or sorbed by the soil. While the portion of the soil near the anode was partially remediated, the soil near the cathode was not.

3.) There appeared to be a correlation between the soil pH and the onset of lead removal. When the pH was reduced to below 4, lead was desorbed from the soil. When the pH was above this critical pH, the soil lead concentration was equal or greater than the initial Pb concentration. The quantity of acid required to reach  $\text{pH} = 4$  was approximately 0.0075 meq/g soil (estimated using Figure 5.1). The source of  $\text{H}^+$  is the water electrolysis reaction in the anode. It was hypothesized that the time required for remediation would decrease if there was an initial source of  $\text{H}^+$  in the anode reservoir (the rationale for conditioning anode with HCl). While the basis for EK flushing termination in the field will be the contaminant soil concentration, these results indicate that extent of contaminant movement in the field can be assessed day-to-day by monitoring the soil pH. This would result in significant cost savings from the reduction in sampling and analytical services. The  $\text{pH}_{\text{critical}}$  is most likely a function of soil and contaminant type thus, it would require determination of site specific parameters. In the future, with additional research and model development, the  $\text{pH}_{\text{critical}}$  may be calculated by examining the soil and contaminant characteristics.

4.) For the majority of the tests that had 1 M acetic acid conditioning of the cathode reservoir, the pH of the last soil section was less than 4. The pH of the soil adjacent to the cathode ("cathode soil") and the number of pore volumes pumped for the acetic acid condition tests are presented in Table 5.13. The pHs of the cathode reservoir liquid for these tests were between 2.3 and 4.6 for the duration of the experiments. However, the pH of the cathode soil was not significantly lower than the initial soil pH (6.5 - 7) unless there was substantial water movement (compare Tests 16 (all) and 20-1 to Test 14, 17, 18, 20-2, and 20-3). This indicates that for acetic acid conditioning, significant decreases in soil pH result from the movement of  $\text{H}^+$  from the anode, not from the cathode. Thus, buffering of the cathode reservoir is most effective if sufficient water movement

occurs. Fortunately, the volume of water transported usually increased when the cathode was conditioned with acetic acid.

**Table 5.13. Cathode Soil pH and Pore Volumes Transported For Test That Had Acetic Acid Conditioning of Cathode Reservoir**

Test No.	Cathode Soil pH	PV Transported
14-1	3.95	11.1
14-2	4.90	8.2
16-1	6.60	1.9
16-2	6.10	3.1
16-3	6.50	0.97
17-1	3.85	22.2
17-2	3.70	25.0
17-3	3.75	22.2
18-1	3.90	25.0
18-2	3.90	27.9
18-3	3.65	24.3
20-1	5.20	1.3
20-2	3.55	4.4
20-3	3.40	12.6

5.) Buffering the cathode with 1 M HAc allowed the desorbed lead to be transported into the cathode reservoir. For the tests that did not have HAc conditioning of the cathode, the desorbed lead resided in the soil near the cathode. Eventually, the  $H^+$  front would have swept across the entire soil sample, lowering the soil pH at the cathode so that the precipitated/sorbed lead could move into the reservoir. However, this would require long durations. Increasing the concentration of  $H^+$  in the cathode (e.g., adding a strong acid) could increase the remediation efficiency by causing a more rapid drop in soil pH ( $H^+$  diffusion from the cathode reservoir would increase as the concentration gradient increased).

6.) The best removal of lead occurred when HCl was added to the anode reservoir (Test 20) despite the fact that for Test 20-1 and 20-2 low flows were observed. The added  $H^+$  (by HCl) was significantly larger than the  $H^+$  produced during the electrolysis of water thus, the soil pH was more rapidly reduced compared to the other tests. Test 20 had the largest  $E_T$  (kW-hr/gallon pumped) thus, increase power costs would result but would be off-set by a decrease in the time required for remediation. Additional research is required before an optimum EK soil flushing design can be determined.

7.) As expected, there was a correlation between pore volumes of water transported and the extent of remediation. Generally, the systems that had the largest flows also experienced the highest lead movement. As mentioned previously,  $H^+$  is transported through the soil by advection and ion migration, lowering the soil pH causing lead desorption. An exception to this observation

was Test 20-1 which had only 1.3 PV of flow but had a significant amount of lead movement. The high concentration of  $H^+$  in the anode increased the transport of  $H^+$  by diffusion thus, less flow was needed.  $Pb^{2+}$  was transported by ion migration. The occurrence of these phenomena affirms the presence of other transport mechanisms (e.g., diffusion, ion migration) and the need for a mechanistic model that predicts EO flow and contaminant transport.

### 5.3.4 Lead Mass Balances

In Table 5.14, the results from mass balance calculations are presented.

**Table 5.14. Lead Mass Balance Results**

Test No.	Test Conditions <sup>1</sup>	Mass of Pb on Soil (mg)		Percent Difference (Initial-Final)	Pb Detected in Cathode Reservoir?
		Initial	Final		
11-1	1000/30/500/500	92.2	94.6	-2.6	No
11-2		110.3	118	-6.9	
11-3		92.0	98.2	-6.7	
12-1	1000/30/DI/DI	103.8	100.8	2.9	No
12-2		104.8	88.4	16	
12-3		107.5	95.4	11	
13-1	150/30/500/500	15.3	16.6	-8.7	No
13-2		15.4	16.1	4.8	
14-1	1000/30/DI/HAc	92.0	64.7	30	Yes
14-2		107.1	104.5	2.4	
15-1	1000/60/500/500	118.5	109.5	7.5	No
15-2		107.0	94.6	12	
15-3		104.6	103.1	1.5	
16-1	150/60/DI/HAc	16.5	14.6	11	No
16-2		14.2	14.7	-3.0	
16-3		14.6	15.7	-7.6	
17-1	1000/60/500/HAc	101.2	25.1	75	Yes
17-2		92.3	17.6	81	
17-3		97.6	22.8	77	
18-1	150/60/500/HAc	18.9	9.9	48	Yes
18-2		18.4	7.6	59	
18-3		18.2	7.4	60	
19-1	150/60/500/500	14.1	17.4	23	No
19-2		13.9	12.9	6.8	
19-3		15.3	14.0	8.3	
20-1	1000/60/HCl/HAc	104.2	104.6	-0.4	Yes
20-2		103.2	16.0	85	
20-3		97.5	5.1	95	

For the tests where lead was not detected in the reservoir in significant amounts (Tests 11, 12, 13, 15, 16, and 19), the average percent difference between the initial and the final soil lead concentration was 8.3 percent. This value represents the extent that the lead mass balance was closed. Closure of a mass balance within 10 percent is considered to be satisfactory. For the tests where a significant amount of lead was moved into the cathode reservoir (Tests 14, 17, 18, and 20), the percent difference represents an estimate of the amount of lead removed from the entire soil system. The lead residing in the cathode reservoir was eventually plated on the electrode (as  $\text{Pb}^0$ ). This phenomenon is demonstrated in Figure 5.24 where the lead concentration in the cathode is plotted versus time for Test 17. At approximately 250 hours a large mass of lead was transported into the cathode reservoir. The subsequent decrease in lead concentration was caused by Pb plating. Rinsing of the cathode electrode with 5 N  $\text{HNO}_3$  accounted for about one-half the missing lead (as calculated by the mass balance). Because the electrodes were not able to be removed from the reactor, complete submersion of the electrode in acid and serial rinses were not possible. In future experiments, the EK reactors will be constructed so that the cathode electrode can be easily removed.

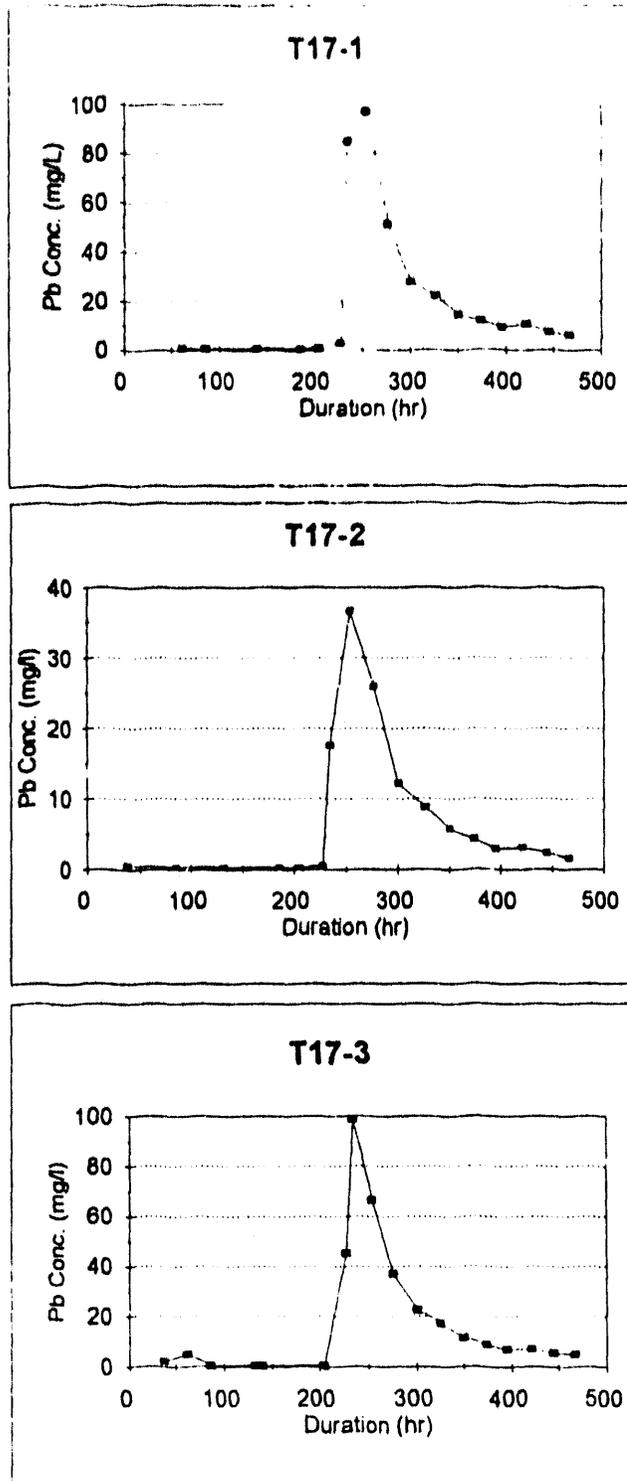


Figure 5.24. Lead Concentration in the Cathode Reservoir Versus Time for Test 17

## 6. CONCLUSIONS

Recently, attention has focused on developing cost effective techniques to remove inorganic contaminants from soils *in-situ*. For most *in-situ* techniques hydraulic pressure (*i.e.*, pumping) is used to disperse the chemical additives and collect the contaminated groundwater. *In-situ* treatment technologies have had success at sites containing sandy soils but have not shown much promise for soils with large amounts of clay and silt (*i.e.* fine grained, low hydraulic conductivity soils). This is due primarily to difficulty in transporting groundwater, contaminants, and chemical additives through the subsurface. Unfortunately, soils high in clay and silt are known to sequester large quantities of inorganic and organic contaminants. Thus, soils having low hydraulic conductivity's are generally efficient in sequestering pollutants but are resistant to standard *in-situ* remediation techniques because of the difficulty in transporting groundwater and contaminants. A candidate technology for the *in-situ* remediation of low permeability soils is electrokinetic (EK) soil flushing. In EK soil flushing, groundwater and contaminants are transported under an applied voltage. The transport of groundwater electroosmotically (*i.e.*, under an applied voltage) does not depend directly on the soil's hydraulic conductivity. Thus, low permeable soils can be remediated *in-situ* if electrokinetics is used as the driving force for liquid and contaminant transport. This report detailed the results from work conducted on the use of electrokinetic (EK) soil flushing to remediate a fine grained (low permeability) soil contaminated with lead.

Water movement during EK soil flushing of a lead contaminated soil was evaluated as a function of EK operating conditions (initial lead concentration (related to initial soil water conductivity), reservoir conditioning (NaNO<sub>3</sub>, acetic acid, HCl), and applied voltage (30 or 60 V)) using the following parameters: Volume of water transported per day, the average current for the duration of the experiment, the volume of soil water transported per amp-hour (K<sub>i</sub>), and the number of kW-hr required to pump one gallon. In all cases, both the flow rate and current increased when the initial lead concentration (and thus soil water conductivity) was increased. An increase in the reservoir waters' conductivity increased both flow and current. Buffering the cathode reservoirs with either NaNO<sub>3</sub> or acetic acid (HAc) while conditioning the anode reservoir with NaNO<sub>3</sub> produced the highest flow rates. Voltage had the largest influence on both the flow rate and current. Increasing the voltage from 30 to 60 V produced a 230 to 330 percent increase in flow and between a 90 and 230 percent increase in current. Increasing the voltage did not cause a noticeable increase in soil temperature or further soil consolidation. In future work, larger voltages should be investigated to determine if an optimum voltage exists.

K<sub>i</sub> and E<sub>T</sub> are measures of how efficient water is transported under an applied voltage. E<sub>T</sub> can be used to compare power costs required for pumping between different operating conditions. A larger K<sub>i</sub> and a smaller E<sub>T</sub> correspond to more efficient water movement. For all cases, the standard deviation from the mean and the coefficients of variation for K<sub>i</sub> and E<sub>T</sub> were smaller than those observed for the flow rate and current because the dependence of flow on current is taken into account when calculating K<sub>i</sub> and E<sub>T</sub>. Thus, determining the effect of initial conditions on EO flow may be more reliable if K<sub>i</sub> and E<sub>T</sub> are used. At higher soil Pb concentrations (soil water conductivity), EO flow was more efficient (larger K<sub>i</sub> and smaller E<sub>T</sub>) for 1000 mg/kg Pb (1400-2000 μmho) compared with 150 mg/kg Pb (650-850 μmho)). Reservoir conditioning had a less

noticeable effect on  $K_j$  and  $E_T$ . An exception was the test where 0.1 N HCl used to condition the anode. This test had a much lower  $K_j$  and much higher  $E_T$ . During the HCl test,  $Cl_2$  (g) was detected olfactory. The production of  $Cl_2$  (g) from  $Cl^-$  requires energy thus,  $Cl_2$  (g) formation could significantly affect  $K_j$  and  $E_T$ . The production of  $Cl_2$  (g) could also present a health and safety problem.

Increasing the voltage increased the volume of water transported per amp-hr ( $K_j$ ) but increased the power required per gallon ( $E_T$ ). The increase in power costs may be offset by a decrease in other costs (personnel, monitoring, *etc*) resulting from a decrease in time required to remediate the site.

Lead removal and soil pH during EK soil flushing were evaluated as a function of initial operating conditions. For tests that did not have cathode reservoir pH control, the pH of the soil segment next to the cathode was higher than the initial pH (pH  $\approx$  8.5 to 9 compared with  $pH_{initial} \approx$  6.5). The  $OH^-$  produced from electrolysis of water in the cathode was transported in the direction opposite of advection by diffusion and ion migration. The  $OH^-$  that is transported into the soil precipitated with the desorbed lead and increased the likelihood of adsorption. Thus, the overall remediation efficiency was decreased. If long EK flushing durations are used, there will be sufficient transport of  $H^+$  to lower the soil pH at the cathode.

There appeared to be a correlation between the soil pH and the onset of lead removal. When the pH was reduced to below 4, lead was desorbed from the soil. When the pH was above this critical pH, the soil lead concentration was equal or greater than the initial Pb concentration. While the basis for EK flushing termination in the field will be the contaminant soil concentration, these results indicate that extent of contaminant movement in the field can be assessed day-to-day by monitoring the soil pH. This would result in significant cost savings from the reduction in sampling and analytical services. The  $pH_{critical}$  is most likely a function of soil and contaminant type thus, it would require determination of site specific parameters. In the future, with additional research and model development, the  $pH_{critical}$  may be calculated by examining the soil and contaminant characteristics.

For the majority of the tests that had 1 M acetic acid (HAc) conditioning of the cathode reservoir, the pH of the last soil section was less than 4. The pHs of the cathode reservoir liquid for these tests were between 2.3 and 4.6 for the duration of the experiments. However, the pH of the cathode soil was not significantly lower than the initial soil pH (6.5 - 7) unless there was substantial water movement. This indicates that for acetic acid conditioning, significant decreases in soil pH results from the movement of  $H^+$  from the anode, not from the cathode. Thus, buffering of the cathode reservoir was most effective if sufficient water movement occurs. Buffering the cathode with 1 M HAc also allowed the desorbed lead to be transported into the cathode reservoir (thus, the soil is truly remediated). For tests that did not have HAc conditioning of the cathode, the desorbed lead resided in the soil near the cathode. Eventually, the  $H^+$  front would have swept across the entire soil sample, lowering the soil pH at the cathode so that the precipitated/sorbed lead could move into the reservoir. However, this would require long durations.

The best removal of lead occurred when HCl was added to the anode reservoir. In one case, 80 percent of the soil-bound lead was removed from 100 percent of the soil (by weight) while 45 percent of the soil (by weight) had more than 95 percent of the lead removed. The HCl tests also

had the largest  $E_T$  (power costs). However, the increase in power costs could be off-set by the decrease time required for remediation. Additional research is required before an optimum EK soil flushing design can be determined.

In summary, EK soil flushing appears to be a promising *in-situ* remediation technique. Significant quantities of lead were removed from the soil in a relatively short period of time when the cathode reservoir was pH controlled. For the tests where there was no pH control, much longer durations were required to move similar amounts of lead. Voltage also strongly affects remediation efficiency. Increasing the voltage from 30 to 60 dramatically increased the efficiency of the EK soil flushing process.

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